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(54) **NON-AQUEOUS ELECTROLYTES FOR ELECTROCHEMICAL CELLS**

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H01M 10/052 (2010.01)

H01M 10/0565 (2010.01)

H01M 10/0567 (2010.01)

H01M 10/0569 (2010.01)

(52) **U.S. Cl.**

CPC **H01M 10/0564** (2013.01); **H01M 10/052** (2013.01); **H01M 10/0565** (2013.01); **H01M 10/0567** (2013.01); **H01M 10/0569** (2013.01); **H01M 2300/0028** (2013.01); **H01M 2300/0082** (2013.01); **Y02E 60/122** (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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(57) **ABSTRACT**

An electrolyte electrochemical device includes an anodic material and an electrolyte, the electrolyte including an organosilicon solvent, a salt, and a hybrid additive having a first and a second compound, the hybrid additive configured to form a solid electrolyte interphase film on the anodic material upon application of a potential to the electrochemical device.

7 Claims, 5 Drawing Sheets

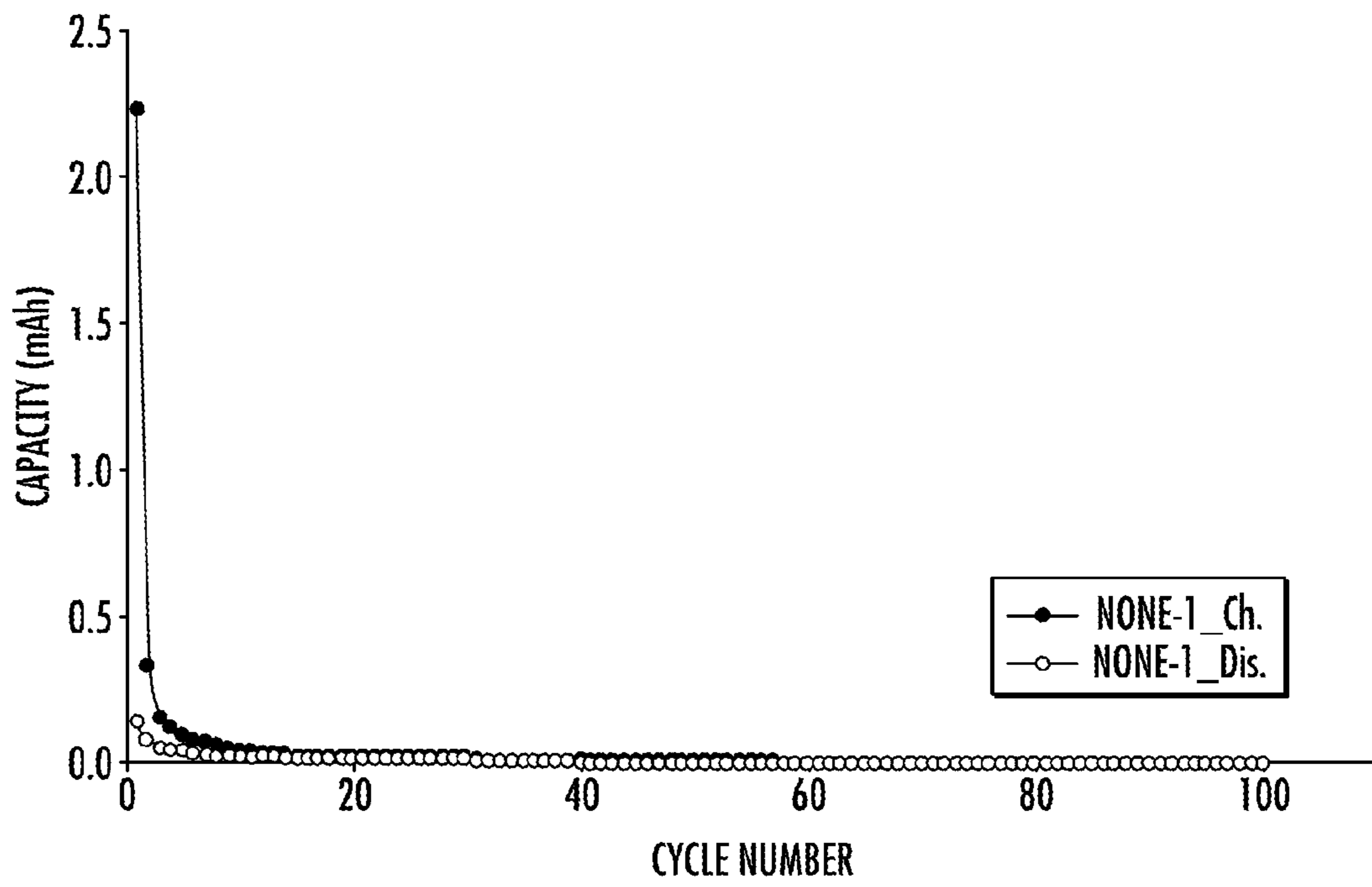


FIG. 1

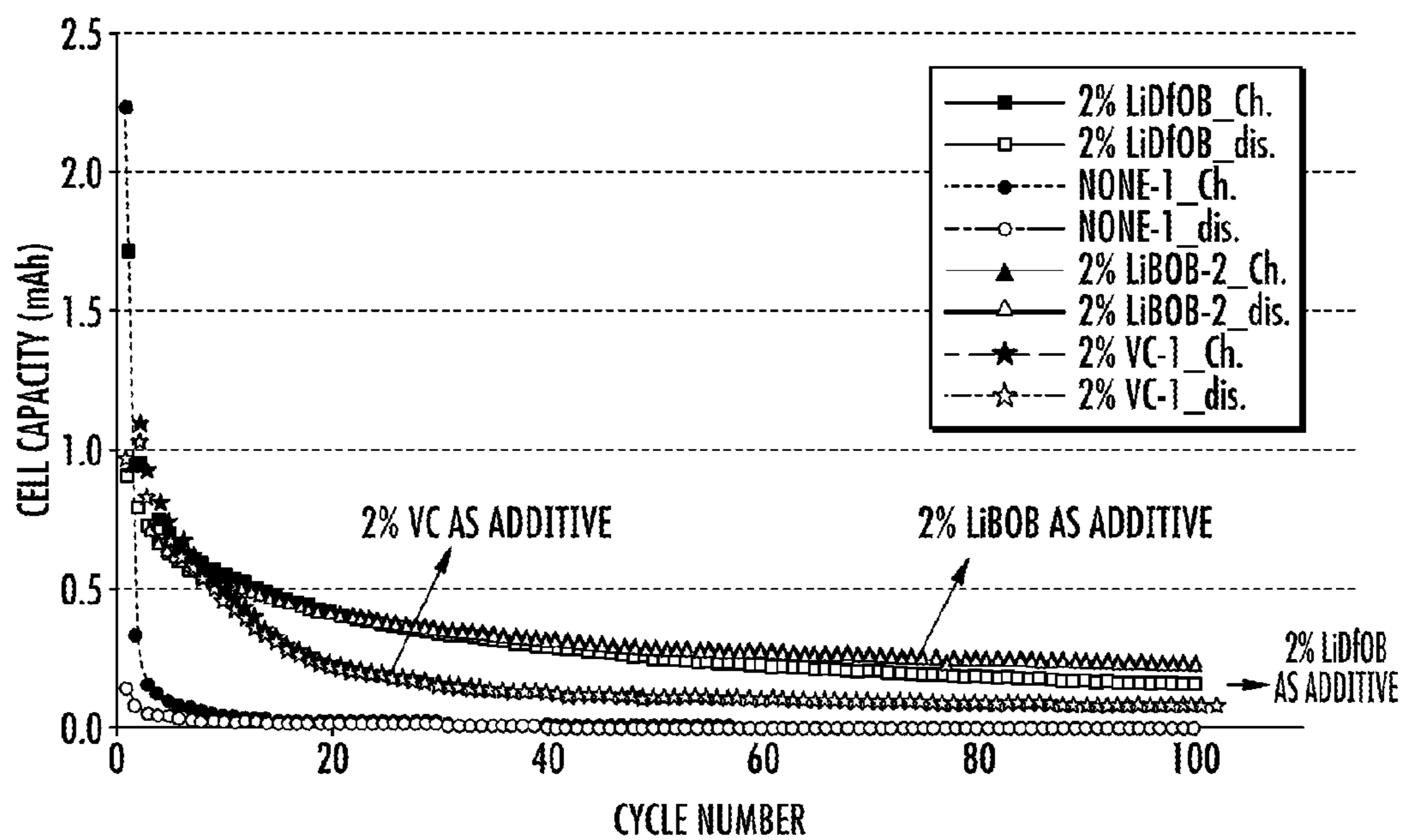


FIG. 2

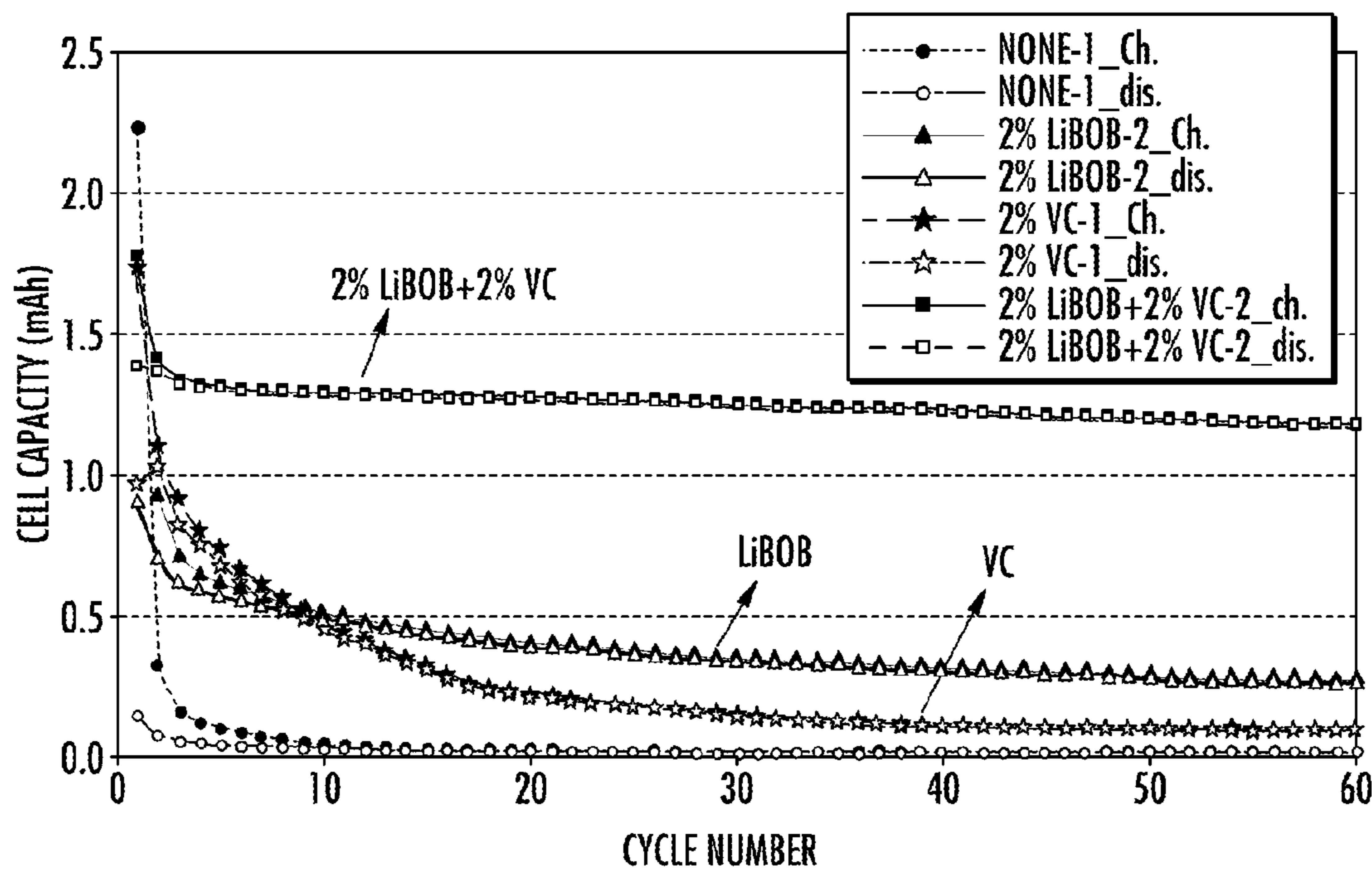


FIG. 3

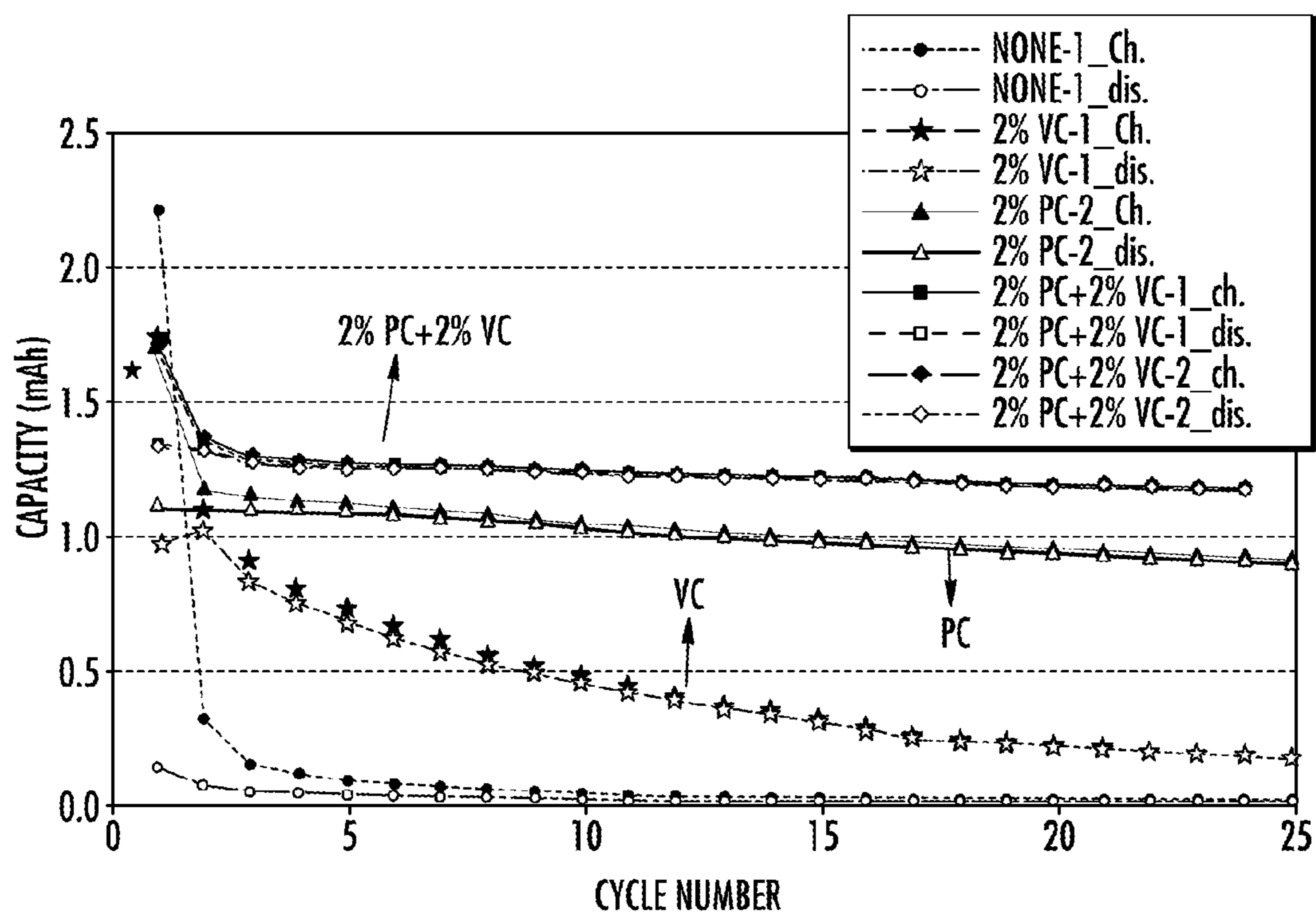


FIG. 4

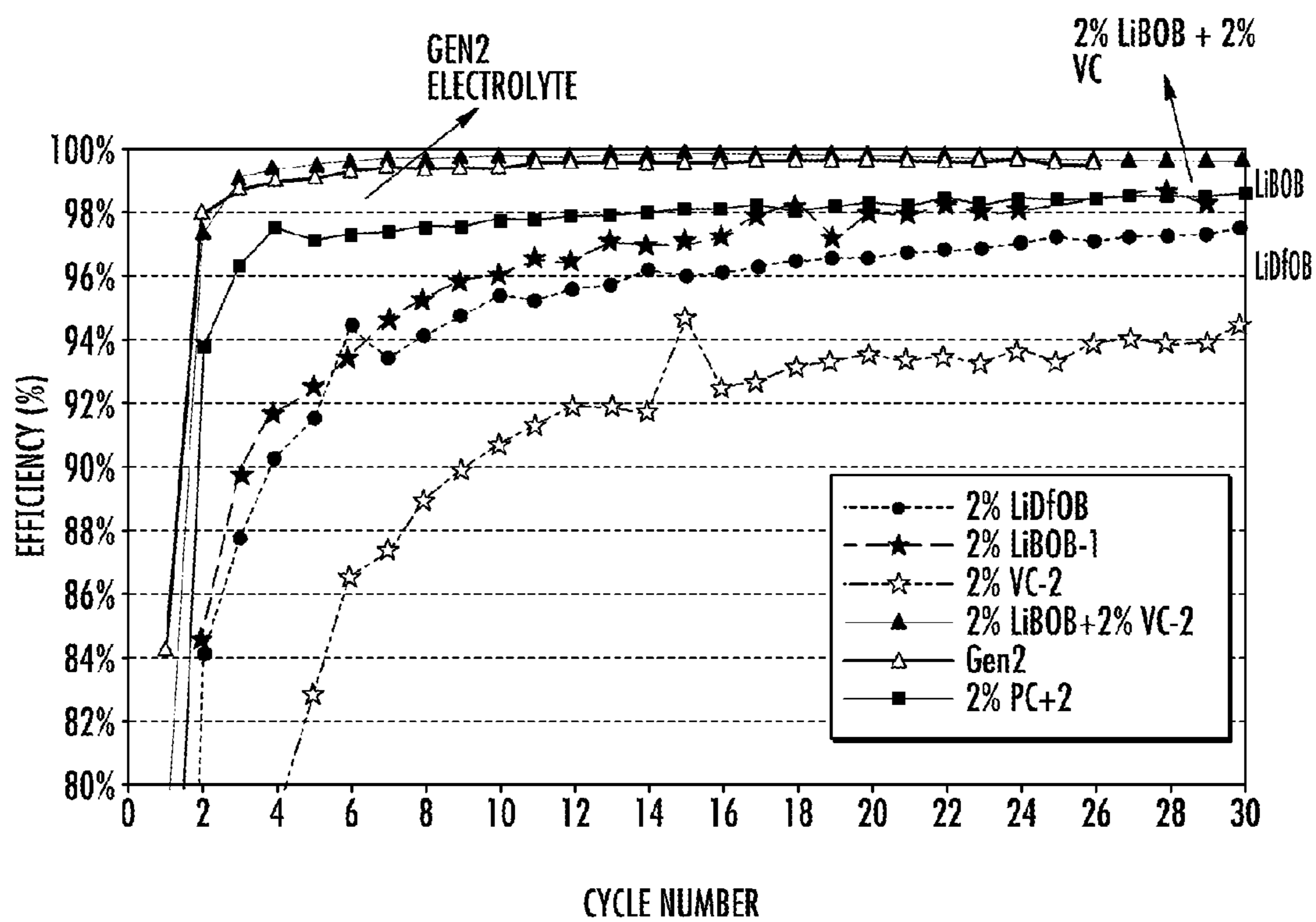


FIG. 5

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NON-AQUEOUS ELECTROLYTES FOR ELECTROCHEMICAL CELLS

GOVERNMENT RIGHTS

The United States Government has rights in this invention pursuant to Contract No. DE-AC02-06CH11357 between the United States Government and UChicago Argonne, LLC, representing Argonne National Laboratory.

FIELD

The present technology is generally directed to non-aqueous electrolyte for electrochemical devices. More particularly, the technology relates to an electrolyte with a hybrid electrolyte additive which is useful to suppress the occurrence of degradation, and an electrochemical device having the same.

BACKGROUND

The increased demand for lithium batteries has resulted in research to improve the cycle life and calendar life of these batteries. Conventional lithium ion batteries typically use non-aqueous electrolytes with a lithium salt such as LiPF_6 dissolved in carboxylic ester solvents such as ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, γ -butyrolactone, etc. The electrolytes are then placed in an electrochemical cell using lithium transition metal oxides as the cathode and carbon or graphite as the anode. Such conventional electrolyte solvents are very flammable and volatile, and can be oxidatively cleaved into gaseous products above 4.4V vs Li/Li^+ . A variety of electrolytes that include silicon-based solvents such as, polysiloxanes and silanes, have been developed to address these issues. However, many secondary batteries that include these solvents exhibit poor capacity and/or cycling performance. There remains a need for a battery that has the safety provided by polysiloxane solvents, but which exhibits acceptable capacity and/or cycling capability.

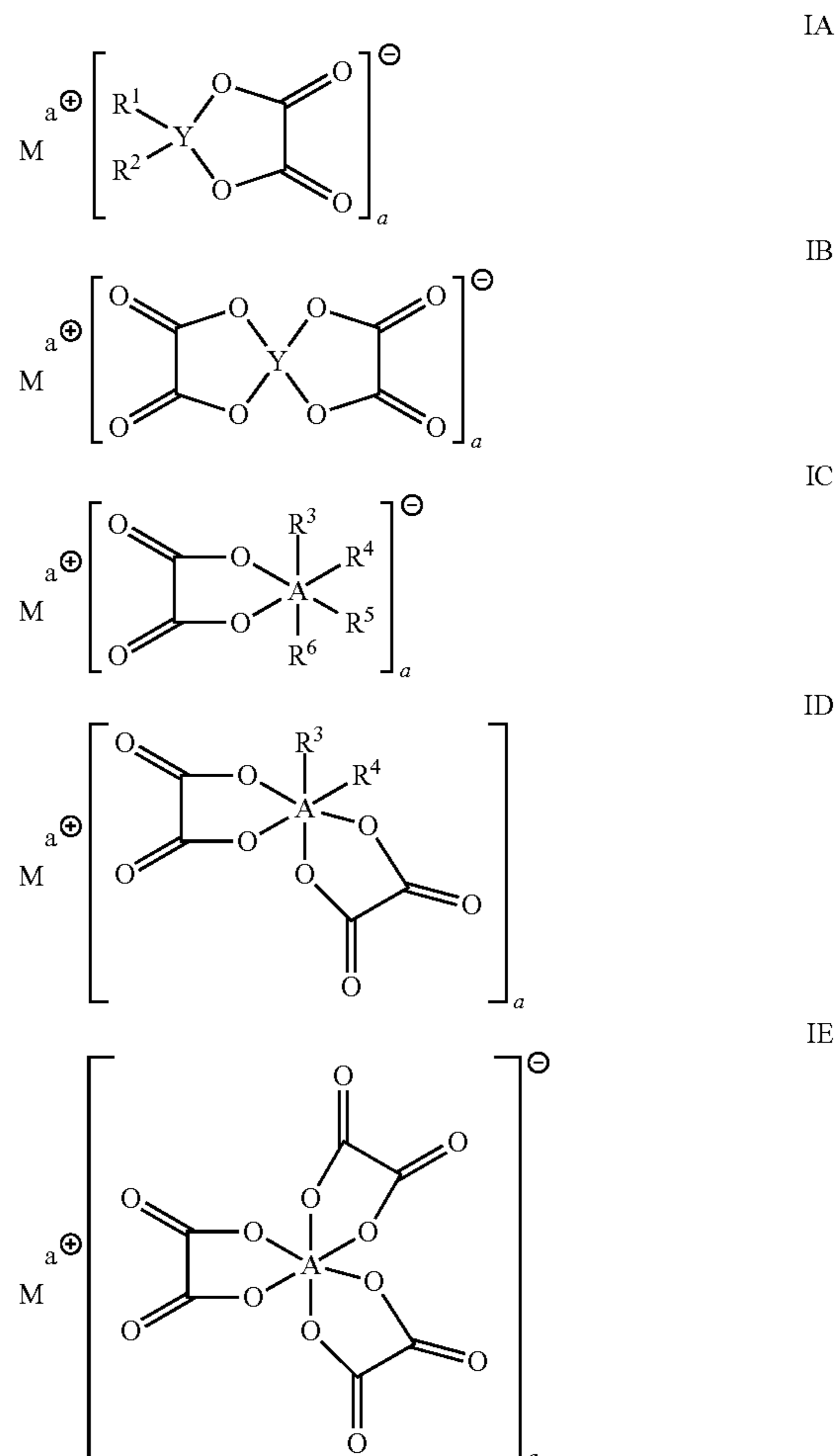
It is generally accepted that electrolyte composition is one of the decisive factors affecting the efficient and long-term operation of Li-ion batteries, as well as their safety for users. The chemical nature of the electrolyte components affects not only lithium ion transport through the electrolyte, but also the structure and composition of a passive layer (often called the solid electrolyte interphase, or SEI) which forms on the carbon anode upon charging. The industry standard electrolyte is ethylene carbonate (EC), which exhibits excellent SEI forming properties, despite its poor, low-temperature performance. Other potential solvents, while having favorable transport properties, may not necessarily provide satisfactory passivation of graphite. For example, propylene carbonate (PC), has been shown to co-intercalate with lithium cations into the crystal structure of graphite, followed by decomposition of the PC. A number of electrolyte additives have developed to address the co-intercalation problem associated, to enable the use of PC-based electrolytes. Other available solvents, such as silanes may be reduced on the surface of the graphite anode and not compatible with graphite anode for the formation of its own SEI. In order to solve the above problems, the use of additives is one effective solution to improve lifetime, capacity, and low temperature performance of a battery. Nevertheless, common additives such as vinylene carbonates, sulfites, sulfates, and phosphates tend to be costly, and only provide for marginal electrolyte improvement.

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SUMMARY

In one aspect, a non-aqueous electrolyte is provided, the electrolyte including a hybrid additive, an aprotic solvent, and a salt. The hybrid additive includes a mixture of at least two compounds, which, during charging of a cell including the electrolyte, are reduced at substantially the same potential to form at least a first and a second reduction product. The potential at which the compounds are decomposed is less than the potential at which the solvent is decomposed, thus preventing solvent decomposition. Upon charging, the first and second reduction products form an integrated and unique SEI, which serves as an efficient protection of a carbon-based anode, thereby providing improved cycling performance and safety compared to a cell without the hybrid additive. The SEI, thus formed, exhibits a synergetic effect on cell performance, that is not observed in a cell with the hybrid additive components individually.

In one aspect, a non-aqueous electrolyte is provided, the electrolyte including a first compound; a second compound; a salt; and a non-aqueous solvent including a silane or siloxane. In the electrolyte, the electrolyte includes about 0.01 wt % to about 5 wt % of the first compound and about 0.01 wt % to about 5 wt % of the second compound. The first compound is represented by Formula I-A, I-B, I-C, I-D or I-E:



and the second compound is represented by Formula II-A, or II-B:

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FIG. 3 is a graph of the cycling performance of a 1.0M LiPF₆ in 1NM3 with 2 wt % LiBOB and 2 wt % VC, according to one example.

FIG. 4 is a cycling performance of 1.0M LiPF₆ in 1NM3 with 2 wt % LiBOB and 2 wt % propylene carbonate (PC), according to one example.

FIG. 5 is columbic efficiency of cell using 1.0M LiPF₆ in 1NM3 with 2 wt % LiBOB and 2 wt % vinyl carbonate, according to one example.

DETAILED DESCRIPTION

In general, "substituted" refers to an organic group as defined below (e.g., an alkyl group) in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to a carbon(s) or hydrogen(s) atom are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group will be substituted with one or more substituents, unless otherwise specified. In some embodiments, a substituted group is substituted with 1, 2, 3, 4, 5, or 6 substituents. Examples of substituent groups include: halogens (i.e., F, Cl, Br, and I); hydroxyls; alkoxy, alkenoxy, alkynoxy, aryloxy, aralkyloxy, heterocyclyloxy, and heterocyclylalkoxy groups; carbonyls (oxo); carboxyls; esters; ethers; urethanes; oximes; hydroxylamines; alkoxyamines; aralkoxyamines; thiols; sulfides; sulfoxides; sulfones; sulfonyls; sulfonamides; amines; N-oxides; hydrazines; hydrazides; hydrazones; azides; amides; ureas; amidines; guanidines; enamines; imides; isocyanates; isothiocyanates; cyanates; thiocyanates; imines; nitro groups; nitriles (i.e., CN); and the like.

Alkyl groups, as used herein, include straight chain and branched alkyl groups having from 1 to about 20 carbon atoms, and typically from 1 to 12 carbons or, in some embodiments, from 1 to 8, 1 to 6, or 1 to 4 carbon atoms. Alkyl groups further include cycloalkyl groups as defined below. Examples of straight chain alkyl groups include those with from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, iso-butyl, sec-butyl, tert-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. Representative substituted alkyl groups can be unsubstituted or substituted.

Cycloalkyl groups, as used herein, are cyclic alkyl groups such as, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group has 3 to 8 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 5, 3 to 6, or 3 to 7. Cycloalkyl groups further include mono-, bi- and poly-cyclic ring systems, such as, for example bridged cycloalkyl groups as described below, and fused rings, such as, but not limited to, decalinyl, and the like. In some embodiments, polycyclic cycloalkyl groups have three rings. Substituted cycloalkyl groups can be substituted one or more times with, non-hydrogen and non-carbon groups as defined above. However, substituted cycloalkyl groups also include rings that are substituted with straight or branched chain alkyl groups as defined above. Representative substituted cycloalkyl groups can be mono-substituted or substituted more than once, such as, but not limited to, 2,2-, 2,3-, 2,4-2,5- or 2,6-disubstituted cyclohexyl groups, which can be substituted with substituents such as those listed above. Cycloalkyl groups can also be bridged cycloalkyl groups in which two or more hydrogen atoms are replaced by an alkylene bridge, wherein the bridge can contain 2 to 6

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carbon atoms if two hydrogen atoms are located on the same carbon atom, or 1 to 5 carbon atoms, if the two hydrogen atoms are located on adjacent carbon atoms, or 2 to 4 carbon atoms if the two hydrogen atoms are located on carbon atoms separated by 1 or 2 carbon atoms. Bridged cycloalkyl groups can be bicyclic, such as, for example bicyclo[2.1.1]hexane, or tricyclic, such as, for example, adamantyl. Representative bridged cycloalkyl groups include bicyclo[2.1.1]hexyl, bicyclo[2.2.1]heptyl, bicyclo[3.2.1]octyl, bicyclo[2.2.2]octyl, bicyclo[3.2.2]nonyl, bicyclo[3.3.1]nonyl, bicyclo[3.3.2]decanyl, adamantyl, noradamantyl, bornyl, or norbornyl groups. Substituted bridged cycloalkyl groups can be unsubstituted or substituted one or more times with non-hydrogen and non-carbon groups as defined above. Representative substituted bridged cycloalkyl groups can be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted adamantyl groups, which can be substituted with substituents such as those listed above.

Alkenyl groups, as used herein, include straight and branched chain and cycloalkyl groups as defined above, except that at least one double bond exists between two carbon atoms. Thus, alkenyl groups have from 2 to about 20 carbon atoms, and typically from 2 to 12 carbons or, in some embodiments, from 2 to 8, 2 to 6, or 2 to 4 carbon atoms. In some embodiments, alkenyl groups include cycloalkenyl groups having from 4 to 20 carbon atoms, 5 to 20 carbon atoms, 5 to 10 carbon atoms, or even 5, 6, 7, or 8 carbon atoms. Examples include, but are not limited to vinyl, allyl, —CH=CH(CH₃), —CH=C(CH₃)₂, —C(CH₃)=CH₂, —C(CH₃)=CH(CH₃), CH=CHCH=CH₂, C(CH₂CH₃)=CH₂, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl, among others. Alkenyl groups may be substituted or unsubstituted. Representative substituted alkenyl groups can be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

Alkynyl groups, as used herein, include straight and branched chain alkyl groups, except that at least one triple bond exists between two carbon atoms. Thus, alkynyl groups have from 2 to about 20 carbon atoms, and typically from 2 to 12 carbons or, in some embodiments, from 2 to 8, 2 to 6, or 2 to 4 carbon atoms. Examples include, but are not limited to —C≡CH, —C≡C(CH₃), —C≡C(CH₂CH₃), —CH₂CCH, —CH₂C≡C(CH₃), and —CH₂C≡C(CH₂CH₃), among others. Alkynyl groups may be substituted or unsubstituted. Representative substituted alkynyl groups can be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

Aryl groups, as used herein, are cyclic aromatic hydrocarbons that do not contain heteroatoms. Aryl groups include monocyclic, bicyclic and polycyclic ring systems. Thus, aryl groups include, but are not limited to, cyclopentadienyl, phenyl, azulenyl, heptalenyl, biphenylenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenyl, anthracenyl, indenyl, indanyl, pentalenyl, and naphthyl groups. In some embodiments, aryl groups contain 5-14 carbons, and in others from 5 to 12 or even 6-10 carbon atoms in the ring portions of the groups. Although the phrase "aryl groups" includes groups containing fused rings, such as fused aromatic-aliphatic ring systems (e.g., indanyl, tetrahydronaphthyl, and the like), it does not include aryl groups that have other groups, such as alkyl or halo groups, bonded to one of the ring members. Rather, groups such as tolyl are referred to as substituted aryl groups. Aryl groups may be substituted or unsubstituted. Representative substituted aryl groups can be mono-substituted or substituted more than once. For

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example, monosubstituted aryl groups include, but are not limited to, 2-, 3-, 4-, 5-, or 6-substituted phenyl or naphthyl groups, which can be substituted with substituents such as those listed above.

Alkoxy groups, as used herein, are hydroxyl groups (—OH) in which the bond to the hydrogen atom is replaced by a bond to a carbon atom of a substituted or unsubstituted alkyl group as defined above. Examples of linear alkoxy groups include but are not limited to methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, and the like. Examples of branched alkoxy groups include but are not limited to isopropoxy, sec-butoxy, tert-butoxy, isopentoxy, isohexoxy, and the like. Examples of cycloalkoxy groups include but are not limited to cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, and the like. Alkoxy groups may be substituted or unsubstituted. Representative substituted alkoxy groups can be substituted one or more times with substituents such as those listed above.

The terms “aryloxy” and “arylalkoxy,” as used herein, refer to, respectively, a substituted or unsubstituted aryl group bonded to an oxygen atom and a substituted or unsubstituted aralkyl group bonded to the oxygen atom at the alkyl. Examples include but are not limited to phenoxy, naphthyl, and benzyloxy. Representative substituted aryloxy and arylalkoxy groups can be substituted one or more times with substituents such as those listed above.

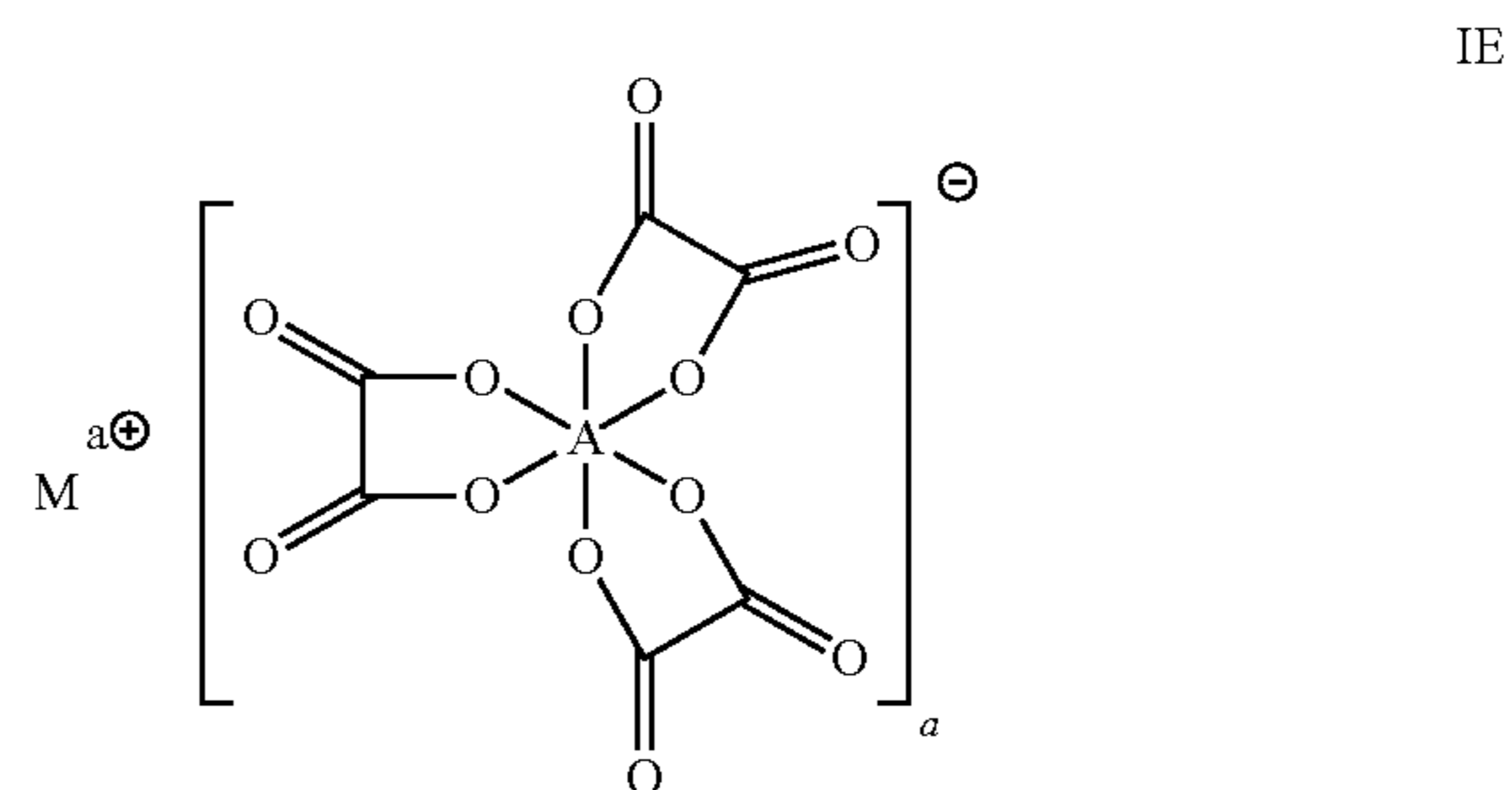
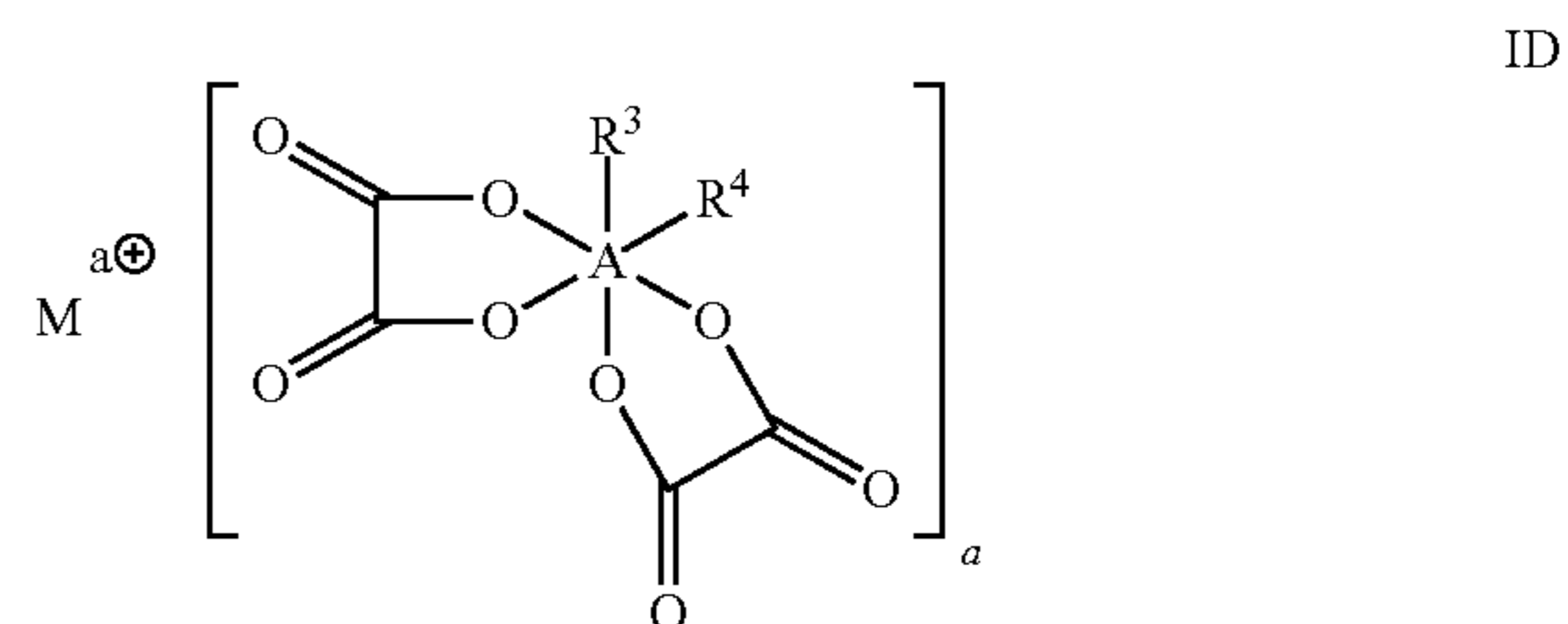
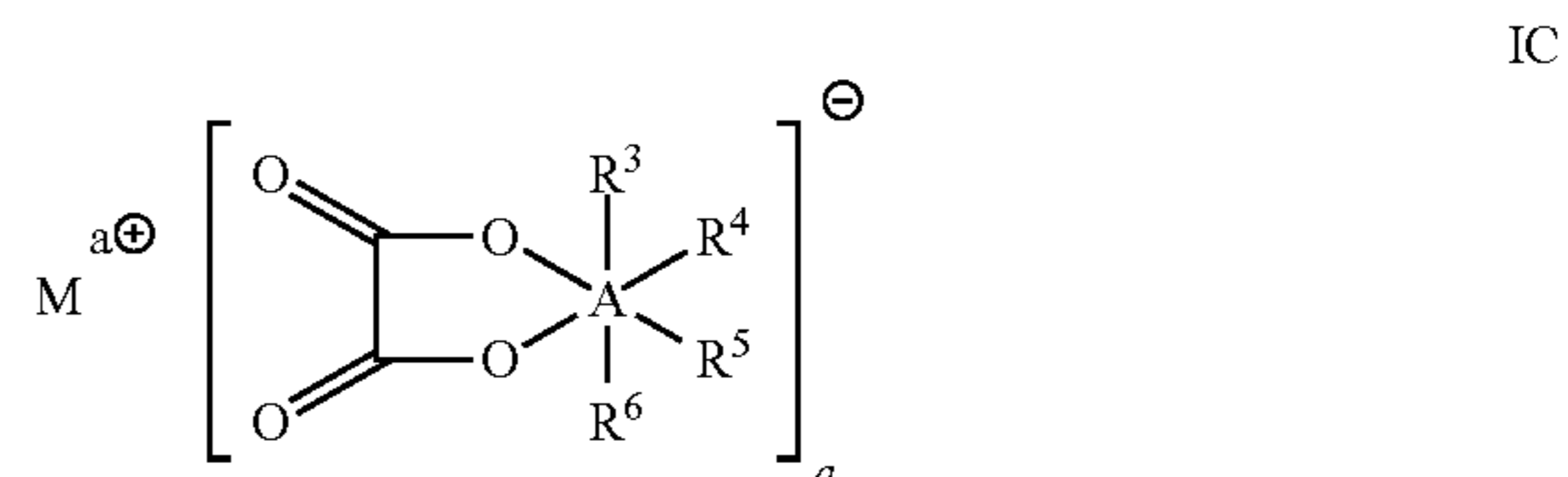
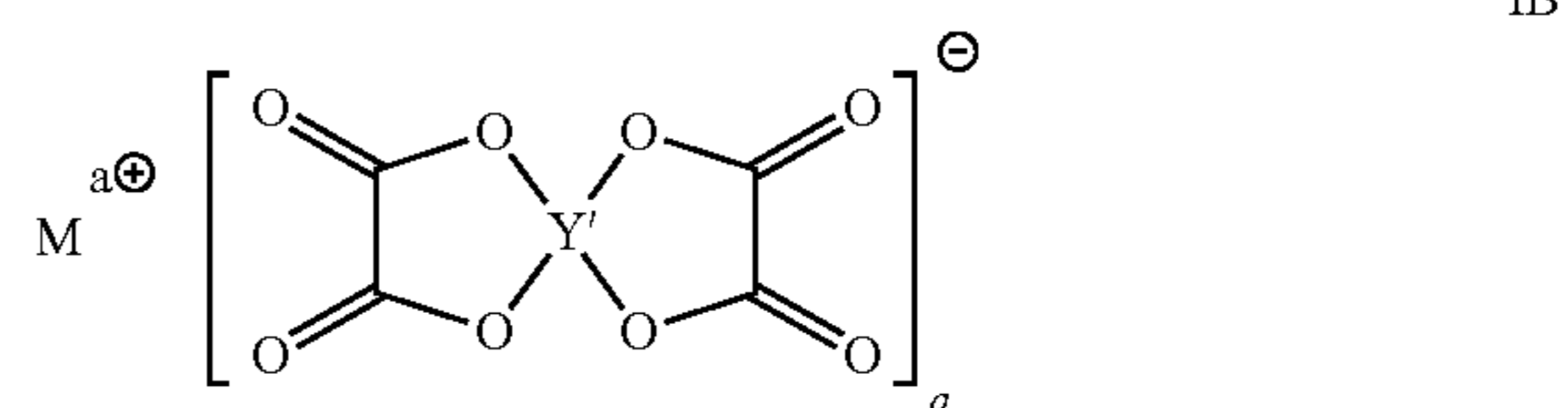
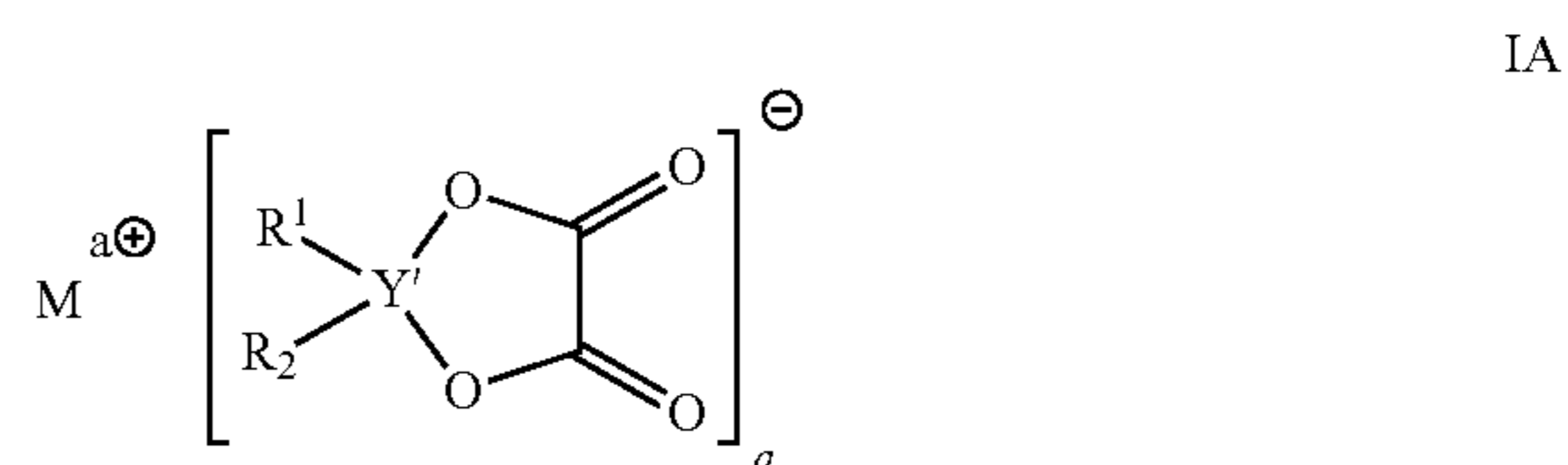
A hybrid electrolyte additive has been found to significantly improve the cyclability and capacity of lithium ion batteries incorporating a silane or siloxane solvent. The hybrid electrolyte additive, which incorporates a first compound and a second compound, and forms a surface electrode interface (SEI) layer on the surface of an anode that includes carbonaceous anode active materials. The SEI layer not only protects the structure of the carbonaceous material, but it can also suppress the occurrence of exfoliation during and charging-discharging cycles, thereby providing for an increase in battery lifetime. Moreover, the hybrid additive can enhance the tolerance of the carbonaceous materials in electrolytes, as well as protecting the carbonaceous material with significantly lower loadings of additives than other materials which for SEI layers. The additives are also useful to slow down the decay of capacity on the cathode during charging-discharging cycles, thereby maintaining the performance of electrochemical devices.

The hybrid additives are believed to form an SEI layer on the surface of an electrode, where the SEI layer is more stable than SEI layers formed by silane or siloxane solvents alone. The enhanced stability of the SEI layer increases the capacity and/or cycling properties of batteries incorporating electrolytes which include the hybrid additives. Additionally, hybrid additives reduce the viscosity of the siloxanes and/or silanes in the solvent. The reduced viscosity improves the wetting of the electrodes in the electrochemical device enough to enhance the homogeneity of the electrolyte distribution in the cell. The enhanced homogeneity also increases the capacity and cycling properties of the batteries. The SEI and the reduced viscosity work either independently or together to enhance the capacity and cycling properties of batteries.

In selection of the silane or siloxane solvent for use in the hybrid electrolyte, as well as the selection of the first and second compounds, the potentials at which the various components decompose are taken into account. The potential at which the first and second compounds are decomposed is less than the potential at which the silane or siloxane solvent is decomposed, thereby preventing solvent decomposition. The decomposition of the first and second compounds provides for the formation of the SEI layer.

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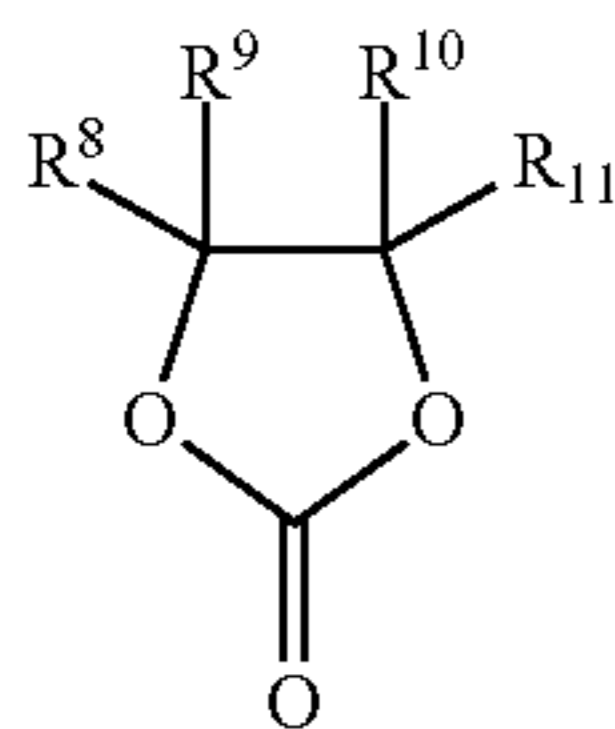
Accordingly, in one aspect, a non-aqueous electrolyte is provided, the electrolyte including a non-aqueous solvent that is a silane or siloxane, a salt, a first compound and a second compound. The electrolyte includes about 0.01 wt % to about 5 wt % of the first compound and about 0.01 wt % to about 5 wt % of the second compound. The first compound is represented as one of Formulas I-A, I-B, I-C, I-D or I-E, or it may be a mixture of any two or more such compounds:



In such compounds, R^1 , R^2 , R^3 , R^4 , R^5 , and R^6 are each independently F, Cl, Br, CN, NO_2 , alkyl, haloalkyl, alkylene, aryl, or haloaryl; M is a metal ion, an ammonium, a phosphonium, a sulfonium, an imidazolium, a pyridinium, or trityl; a is 1, 2, 3, or 4; Y' is B or Al; and A is P or As. The second compound of the electrolyte is represented by Formula II-A, or II-B:



-continued



In such compounds, R^8 , R^9 , R^{10} , and R^{11} are each independently selected from H, F, Cl, Br, CN, NO_2 , alkyl, haloalkyl, alkylene, aryl, or haloaryl.

According to some embodiments, the second compound is represented by Formula II-B, wherein at least one of R^8 and R^{10} is a fluorinated alkyl. The fluorinated alkyl, in some embodiments is a C_1 - C_8 fluorinated alkyl group. Illustrative examples include, but are not limited to, CF_3 , CF_3CH_2 , CF_3CF_2 , $\text{CF}_3\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2$, $\text{CF}_3\text{CH}_2\text{CF}_2$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2$, HCF_2 , HCF_2CH_2 , HCF_2CF_2 , $\text{HCF}_2\text{CH}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CH}_2$, $\text{HCF}_2\text{CH}_2\text{CF}_2$, $\text{HCF}_2\text{CF}_2\text{CH}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2$, $\text{HCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CF}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2$, FCH_2 , FCH_2CH_2 , FCH_2CF_2 , $\text{FCH}_2\text{CF}_2\text{CH}_2$, $\text{FCH}_2\text{CF}_2\text{CF}_2$, $\text{CH}_3\text{CF}_2\text{CH}_2$, $\text{CH}_3\text{CF}_2\text{CF}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_2$, $\text{CH}_3\text{CF}_2\text{CF}_2\text{CF}_2$, $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2$, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2$, $\text{CH}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CH}_2$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$ or $\text{HCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$.

According to some embodiments, the first compound is a compound of Formula I-A or I-B. In the first compound, R^1 and R^2 may be independently F, Cl, Br, CN, C_1 - C_6 alkyl, or C_1 - C_6 haloalkyl. In the first compound M may be a metal ion, an ammonium, a phosphonium, a sulfonium, an imidazolium, a pyridinium, or trityl group. Illustrative metals and ammonium ions include, but are not limited to, Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cs^+ , Ag^+ , Zn^{2+} , Cu^+ , Cu^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Mn^{2+} , Ti^{2+} , Ti^{3+} , Ti^{4+} , Pb^{2+} , Cr^{3+} , V^+ , V^{2+} , Ru^{2+} , Ru^{3+} , Y^{3+} , a lanthanide, an actinide, or a group represented as $[\text{NR}^7_4]^+$ wherein each R^7 is independently, H, methyl, ethyl, propyl, or butyl. In some embodiments, M is Li^+ , Na^+ , or K^+ . In some embodiments, Y' is B.

According to some embodiments, the second compound is represented by Formula II-B, R^8 is a fluorinated alkyl or a fluorinated alkoxy; R^9 and R^{10} are individually H, F, Cl, CF_3 or CH_3 ; and R^{11} is H, F, Cl or an alkyl group.

In one embodiment, the electrolyte includes a first compound that is $\text{Li}[\text{B}(\text{C}_2\text{O}_4)_2]$ and a second compound that is vinylene carbonate. In another embodiment, the electrolyte includes a first compound that is $\text{Li}[\text{BF}_2(\text{C}_2\text{O}_4)]$ and a second compound that is vinylene carbonate.

In any of the above embodiments, the electrolyte includes about 1 wt % to about 3 wt % of the first compound, and about 1 wt % to about 3 wt % of the second compound. In any of the above embodiments, the electrolyte includes about 2 wt % of the first compound, and about 2 wt % of the second compound.

II-B

In any of the above embodiments of the electrolyte, the non-aqueous solvent may include a silane, or a siloxane that is a monosiloxane, disiloxane, a trisiloxane, a tetrasiloxane, a polysiloxane or a mixture of any two or more such solvents. In some embodiments of the electrolyte, the non-aqueous solvent includes a disiloxane, a trisiloxane, or a tetrasiloxane, or a mixture of any two or more such solvents. Tetrasiloxanes, trisiloxanes and disiloxanes may provide for electrolytes with a lower viscosity than electrolytes that include similarly structured polysiloxanes. The reduced viscosity can further improve wetting of electrodes in an electrochemical device, which enhances the homogeneity of the electrolyte distribution in an electrochemical cell incorporating the electrolyte. Surprisingly, the enhanced homogeneity may be sufficient to increase the capacity and cycling properties of batteries. For instance, when the device is repeatedly cycled between about 2.7 V and 4.0 V, using a charge and discharge rate of 0.1 C after formation of a passivation layer on the anode, the electrolytes provide a secondary battery having a discharge capacity retention greater than 90% at cycle number 200.

As noted above, the non-aqueous solvent may include a silane. Silanes typically have a viscosity that is reduced relative to similarly structured polysiloxanes, tetrasiloxanes, trisiloxanes or disiloxanes. The lower viscosity of the silanes may further improve wetting of electrodes in an electrochemical device enough to further increase the capacity and cycling properties of batteries. For instance, when the device is repeatedly cycled between 2.7 V and 4.0 V using a charge and discharge rate of 0.2 C after formation of a passivation layer on the anode, these electrolytes may provide a secondary battery having a discharge capacity retention greater than 90% at cycle number 400.

The tetrasiloxanes, trisiloxanes, disiloxanes and/or silanes also provide an electrolyte with high ionic conductivities in addition to enhanced cycling properties. For instance, one or more of the silicon atoms in the tetrasiloxanes, trisiloxanes, disiloxanes and/or silanes may be linked to a first substituent that includes a poly(alkylene oxide) moiety. The poly(alkylene oxide) moieties assist in dissolution of lithium salts employed in the electrolyte. Accordingly, the tetrasiloxanes, trisiloxanes, disiloxanes and/or silanes may provide an electrolyte with a concentration of free ions suitable for use in batteries. Additionally, the poly(alkylene oxide) moieties enhance the ionic conductivity of the electrolyte at room temperatures. For instance, silanes having a poly(alkylene oxide) moiety may provide an electrolyte with an ionic conductivity that is greater than 1×10^{-3} S/cm at 25° C. In some embodiments, the conductivity is greater than 5×10^{-3} S/cm at 37° C. In some embodiments, the conductivity is from about 1×10^{-3} S/cm to about 1×10^{-2} S/cm at 25° C. At these performance levels, the electrolytes are suitable for use in batteries such as high-energy and long cycle life lithium secondary batteries, satellite applications, and biomedical devices such as defibrillators.

Additionally or alternately, one or more of the silicons in the tetrasiloxanes, trisiloxanes, disiloxanes and/or silanes may be linked to a second substituent that includes a cyclic carbonate moiety. The cyclic carbonate moieties may be capable of dissolving the salts that are employed in battery electrolytes. As a result, the carbonates can provide high concentrations of free ions in the electrolyte, and accordingly, increase the ionic conductivity of the electrolyte. For instance, such silanes with a cyclic carbonate moiety may provide an electrolyte with an ionic conductivity of greater than 1×10^{-3} S/cm at 25° C., or higher than 5×10^{-3} S/cm at 37° C.

According to some embodiments, the siloxanes and/or silanes include one or more oligo(ethylene glycol)-substi-

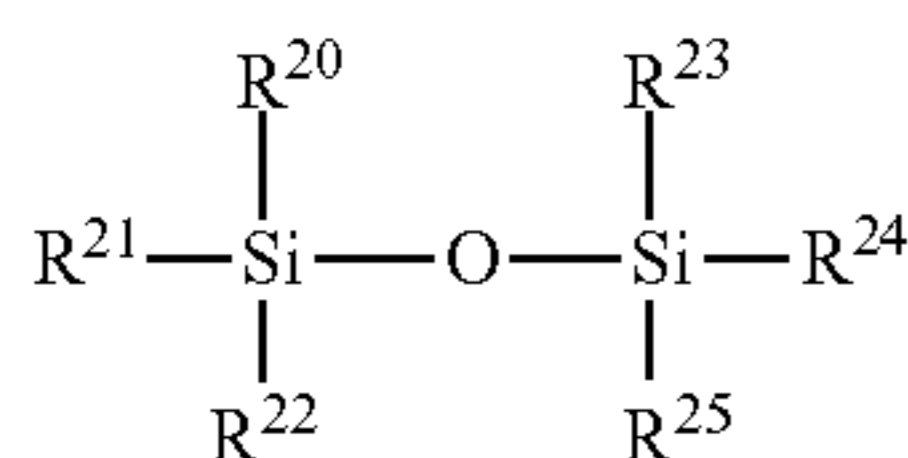
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(CH₂CH₂O)₃CH₃], (CH₃)₂Si[O(CH₂CH₂O)₄CH₃][(CH₂)₃O(CH₂CH₂O)₄CH₃], or (CH₃)₂Si[O(CH₂CH₂O)₅CH₃][(CH₂)₃O(CH₂CH₂O)₅CH₃]; and mixtures of any two or more such compounds.

In one embodiment, the non-aqueous electrolyte solvent includes a disiloxane compound. Suitable disiloxanes include a backbone with a first silicon and a second silicon. The first silicon is linked to a first substituent that includes an oligo(alkylene glycol) moiety or a cyclic carbonate moiety. For instance, the first silicon can be selected from a group consisting of a first side-chain that includes an oligo(alkylene glycol) moiety, a first side-chain that includes a cyclic carbonate moiety or a cross-linker that includes a oligo(alkylene glycol) moiety which cross-links the disiloxane to a second siloxane. In some instances, the disiloxanes include no more than one oligo(alkylene glycol) moiety and/or no more than one cyclic carbonate moiety. For instance, the entities linked to the first silicon and the second silicon, other than the first substituent, can each exclude an oligo(alkylene glycol) moiety and/or a cyclic carbonate moiety. In some instances, the disiloxane excludes an oligo(alkylene glycol) moieties or excludes cyclic carbonate moieties. In some embodiments, the inorganic salt is a lithium salt.

The second silicon can be linked to a second substituent that is a second side-chain that includes an oligo(alkylene glycol) moiety and a second side-chain that includes a cyclic carbonate moiety. In some instances, the disiloxanes include no more than two oligo(alkylene glycol) moieties and/or no more than two cyclic carbonate moieties. For instance, the entities linked to the first silicon and the second silicon, in addition to the first substituent and the second substituent, can each include an oligo(alkylene glycol) moiety and/or a cyclic carbonate moiety.

In some embodiments, the disiloxanes are represented by Formula V:



Formula V

where R²⁰, R²², R²³ and R²⁵ are individually an alkyl group or an aryl group; R²¹ is an alkyl group, an aryl group, an oligo(alkylene glycol) group, or an alkylcyclic carbonate group; and R²⁴ is an alkyl group, an aryl group, an oligo(alkylene glycol) group, an alkylcyclic carbonate group, Group I, Group II, or Group III. In some embodiments, R²¹ is selected from Group I, Group II, or Group III. In other embodiments, R²⁴ is an alkyl group, an aryl group, Group I, or Group III. In some embodiments, R²⁴ is selected from Group I or Group III. In some embodiments, R²¹ is selected from an alkyl group, an aryl group, or Group I. In other embodiments, R²¹ is an alkyl, an aryl, or Group III. In some embodiments, R²⁰, R²², R²³, and R²⁵ are individually an alkyl group. For example, R²⁰, R²², R²³ and R²⁵ may individually be a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, or tert-butyl group. In some embodiments, R²⁰, R²², R²³, and R²⁵ are each a methyl group.

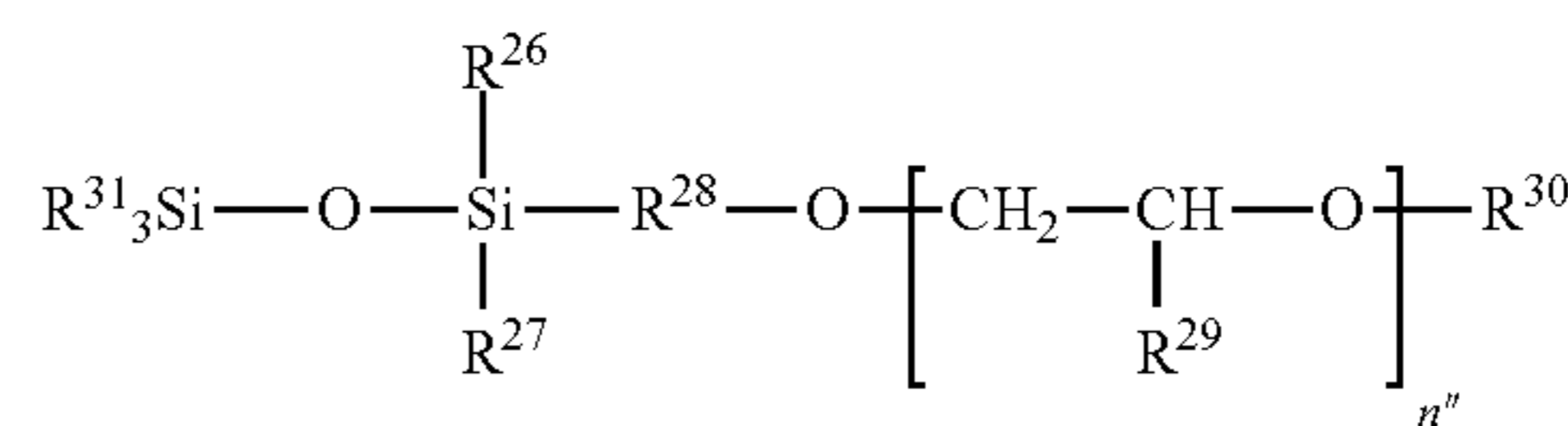
In one example of the disiloxane, the first substituent is a side chain that includes an oligo(alkylene glycol) moiety. The oligo(alkylene glycol) moiety can include an oxygen linked directly to the first silicon. For instance, the disiloxanes can be represented by Formula V, where R²⁴ is a Group I, and R¹⁵ is a bond. Alternately, a spacer can link the oligo(alkylene gly-

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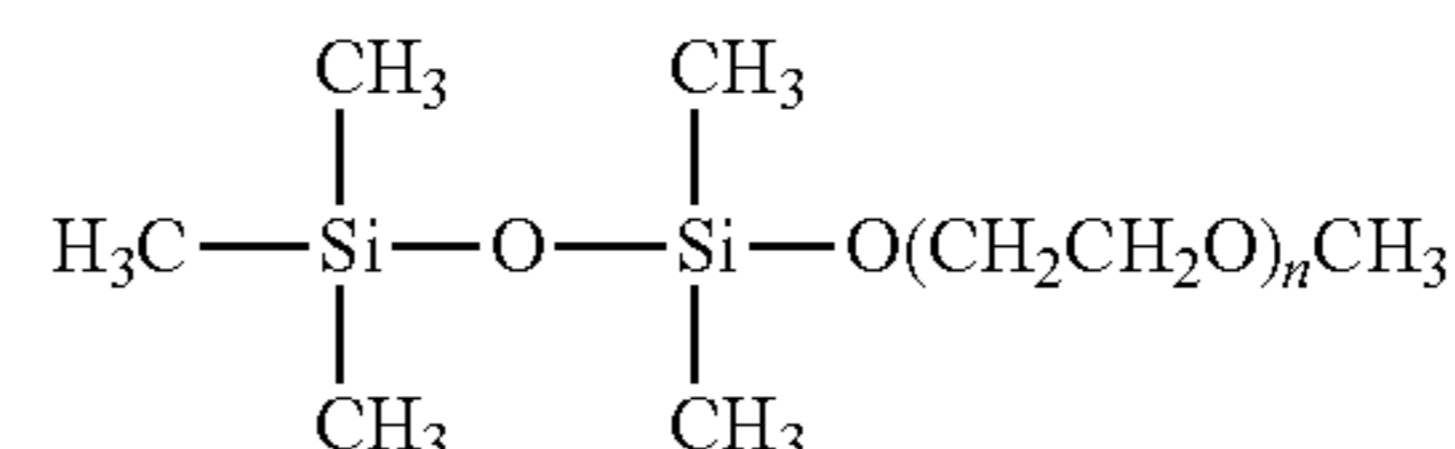
col) moiety to the first silicon. For instance, the disiloxanes can be represented by Formula V, where R²⁴ is Group I, and R¹⁵ is a divalent organic moiety. Where the first substituent is a side chain that includes an oligo(alkylene glycol) moiety, each of the entities linked to the second silicon can be alkyl groups and/or aryl groups. For instance, the second substituent can be an alkyl group or an aryl group. In some embodiments, the disiloxane is a compound of Formula V, where R²¹ is Group I, and R¹⁸ is an alkyl group or an aryl group.

Exemplary compounds of Formula V, include, but are not limited to:

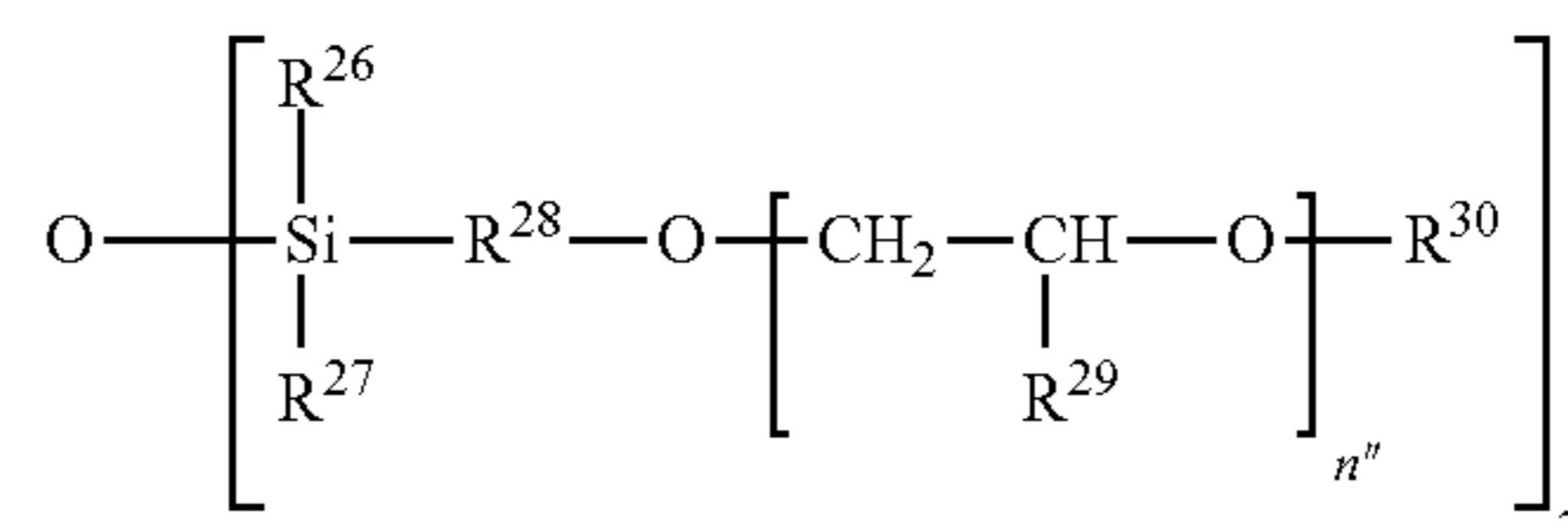
Formula V-A



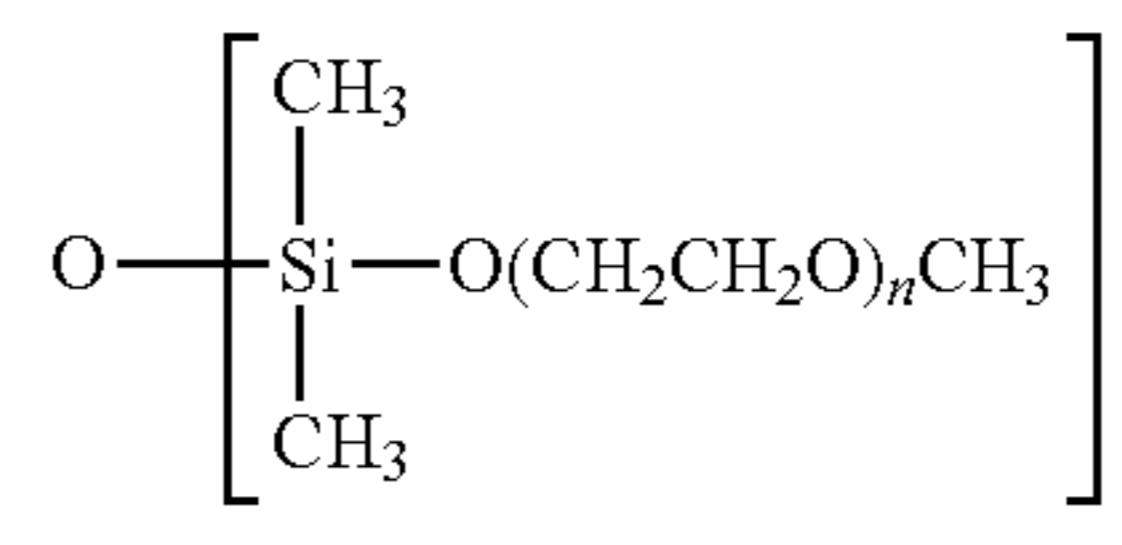
Formula V-B



Formula V-C



Formula V-D



In the above compounds of Formulas V-A, V-B, V-C, and V-D, each R²⁶ and R²⁷ are individually an alkyl group or an aryl group; each R²⁸ is a bond or a divalent spacer; each R²⁹ is individually a hydrogen atom or an alkyl group; each R³⁰ is individually an alkyl group; each R³¹ is individually an alkyl group or an aryl group; n is an integer from 0 to 15, and n'' is an integer from 1 to 30. In some embodiments, n is an integer from 1 to 12. Where R²⁸ is a divalent spacer, it may be an organic divalent spacer, such as an alkylene, an alkylene glycol, or a bivalent ether group. For example, R²⁸ may be a moiety having one or more methylene groups. In some embodiments, R²⁸ is methylene, ethylene, propylene, or butylene. In one embodiment, R²⁸ is —(CH₂)₃—. In some embodiments, R²⁸ may be partially or completely halogenated. For instance, the above spacers can be completely or partially fluorinated. In some embodiments, each R³¹ is individually an alkyl group. For example, each R³¹ may individually be a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, or tert-butyl group. In some embodiments, each R³¹ is a methyl group. In one embodiment, each R³¹ is a methyl, R²⁸ is —(CH₂)₃—; and R²⁹ is a hydrogen. In one embodiment, each R³¹ is a methyl; R²⁸ is —(CH₂)₃—; and R²⁹ is a hydrogen; and n is 3. In some embodiments, n is 3.

In some embodiments, the disiloxane compound is a compound of formula CH₃O(CH₂CH₂O)_nSi(CH₃)₂OSi(CH₃)₂O(CH₃)₂SiO(CH₂CH₂O)_nCH₃, CH₃O(CH₂CH₂O)_n(CH₂)₃Si(CH₃)₂OSi(CH₃)₂O(CH₃)₂Si(CH₂)₃O(CH₃)₂Si(OCH₂CH₂)_nOCH₃, [(CH₃)₃SiO]₂Si(CH₃)O(CH₂CH₂O)_nCH₃,

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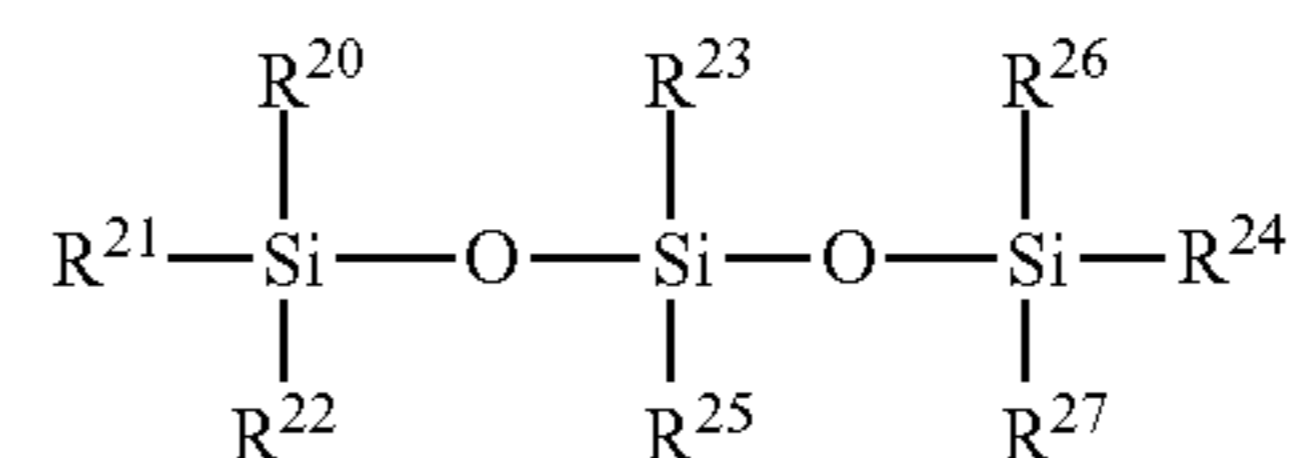
$[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_3)\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $\text{R}-\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}-\text{R}$, $\text{R}-\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$, $\text{R}-\text{O}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{OR}$, $\text{R}-\text{O}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$; $\text{R}-\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2)_n\text{CH}_3$, or $\text{R}-\text{O}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2)\text{CH}_3$, where n is 2, 3, 4, 5, 6, or 7; and R is a carbonate group. Specific examples may include, but are not limited to $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2-\text{Si}(\text{CH}_3)_3\text{O}(\text{CH}_3)_2\text{Si}-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7(\text{CH}_2)_3-\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}-(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$.

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and $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$, or a mixture of any two or more such compounds.

In some embodiments, the non-aqueous electrolyte solvent includes a trisiloxane compound. Some such trisiloxanes may be represented by general Formula VI:

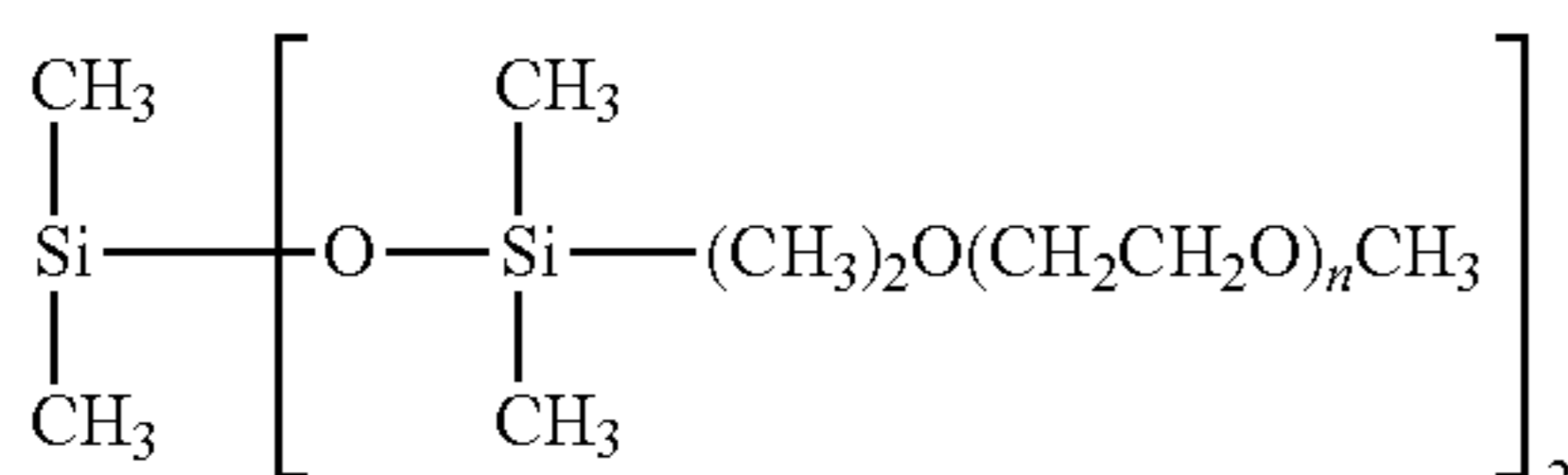
Formula VI



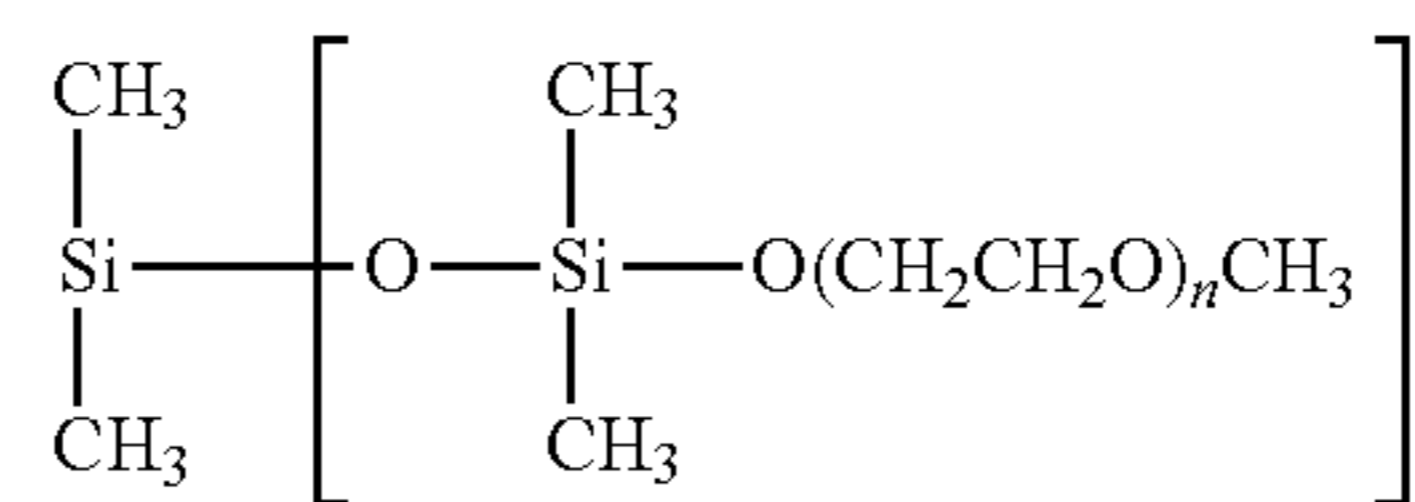
where R^{20} , R^{22} , R^{23} , R^{24} , R^{26} and R^{27} are individually an alkyl group or an aryl group; R^{21} is an alkyl group, an aryl group, an oligo(alkylene glycol) group, or an alkylcyclic carbonate group; and R^{24} is an alkyl group, an aryl group, an oligo(alkylene glycol) group, or an alkylcyclic carbonate group. In some embodiments, R^{21} is selected from Group I, Group II, or Group III. In other embodiments, R^{24} is an alkyl group, an aryl group, Group I, or Group III. In some embodiments, R^{24} is selected from Group I or Group III. In some embodiments, R^{21} is selected from an alkyl group, an aryl group, or Group I. In other embodiments, R^{21} is an alkyl, an aryl, or Group III. In some embodiments, R^{20} , R^{22} , R^{23} , R^{24} , R^{26} and R^{27} are individually an alkyl group. For example, R^{20} , R^{22} , R^{23} , R^{24} , R^{26} and R^{27} may individually be a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, or tert-butyl group. In some embodiments, R^{20} , R^{22} , R^{23} , R^{24} , R^{26} and R^{27} are each a methyl group.

Representative trisiloxanes of Formula VI include, but are not limited to, those compounds described by Formulas VI-A, VI-B, VI-C, and VI-D.

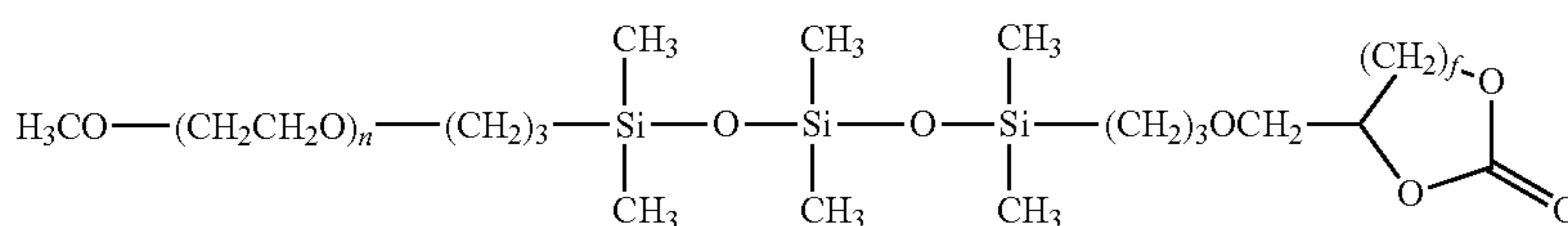
Formula VI-A



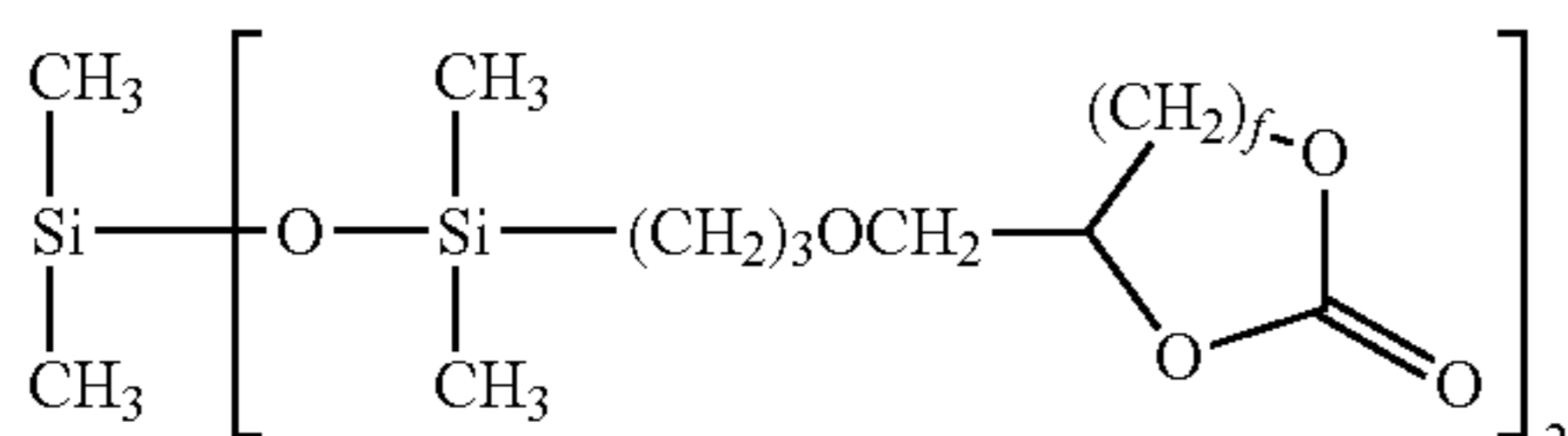
Formula VI-B



Formula VI-C



Formula VI-D



$(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{O}$
 $(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$,
 $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}$
 $(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}$
 $(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$,

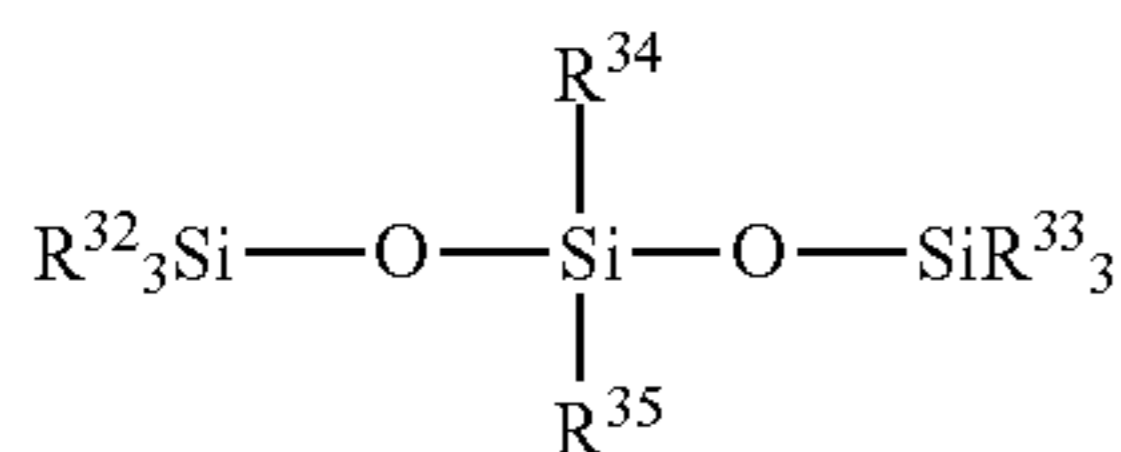
In each of the formulas, each n is independently an integer from 1 to 12 and f is 1 or 2.

In each of Formulas VI-A and VI-B, a trisiloxane having terminal silicon atoms linked to a side chain that includes a poly(ethylene oxide) moiety are shown. Formula VI-A illustrates an organic spacer positioned between each poly(ethylene oxide) moiety and the terminal silicon. Formula VI-B illustrates each of the terminal silicon atoms linked directly to a poly(ethylene oxide) moiety. In each of Formulas VI-C and VI-D a trisiloxane with a terminal silicon linked to a side chain that includes a cyclic carbonate moiety are shown. Formula VI-C illustrates one of the terminal silicon atom linked to a side chain that includes a cyclic carbonate moiety and one of the terminal silicon atoms linked to a side chain

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that includes a poly(ethylene oxide) moiety. Formula VI-D illustrates each of the terminal silicon atoms linked to a side chain that includes a cyclic carbonate moiety.

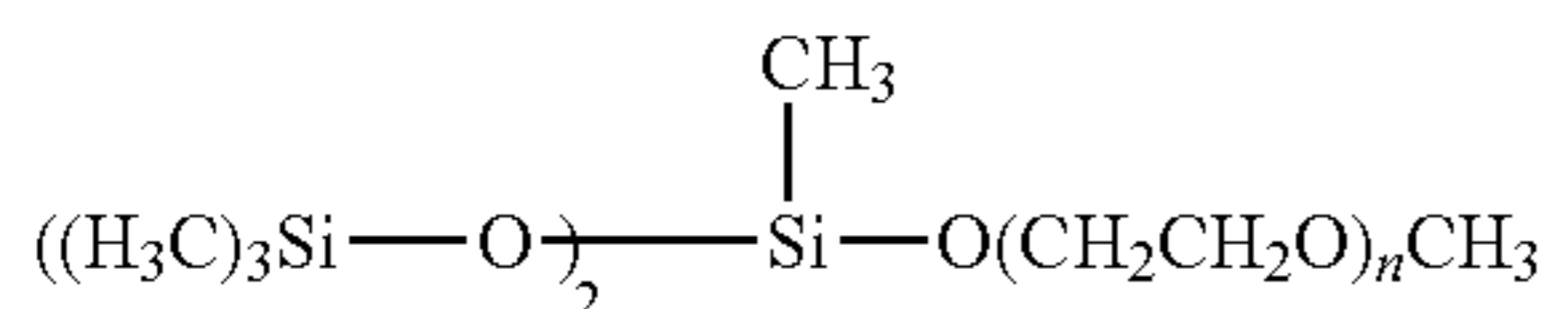
In other embodiments, the trisiloxanes are compounds according to Formula VII.



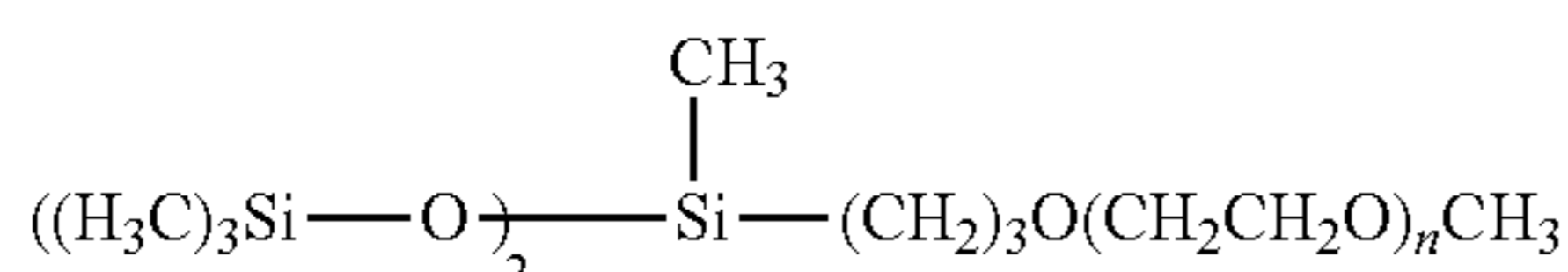
Formula VII

where each R^{32} , R^{33} , and R^{34} are individually an alkyl group or an aryl group; and R^{35} is selected from Group I, Group II, or Group III.

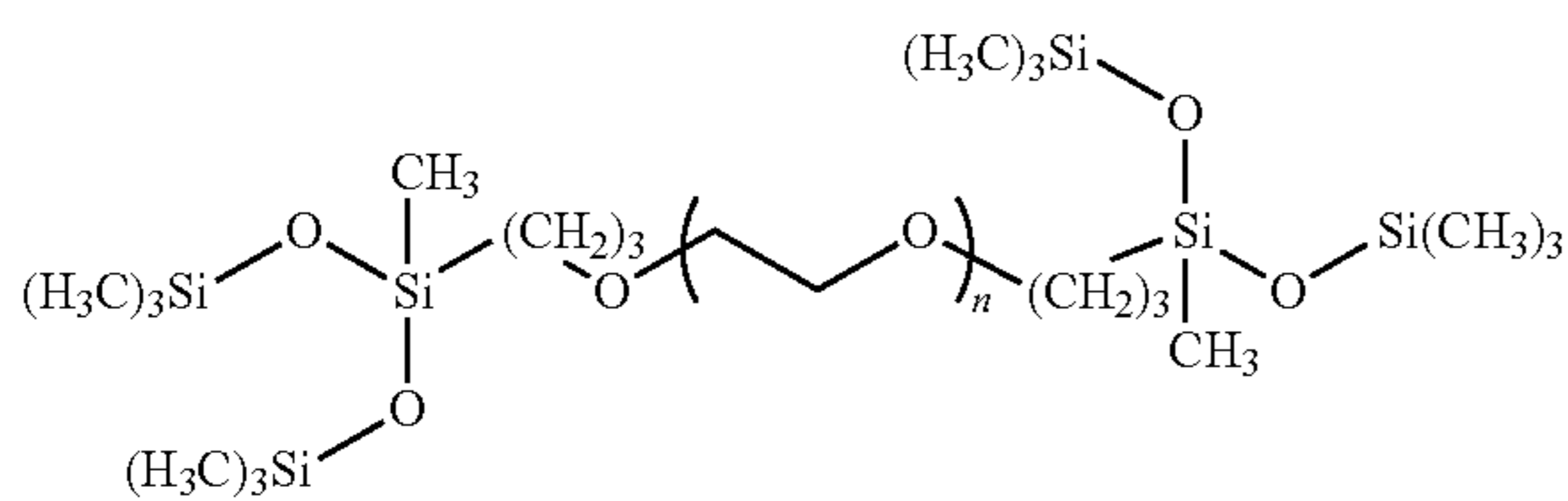
Representative compounds of Formula VII include, but are not limited to compounds such as those of Formulas VII-A, VII-B, VII-C and VII-D.



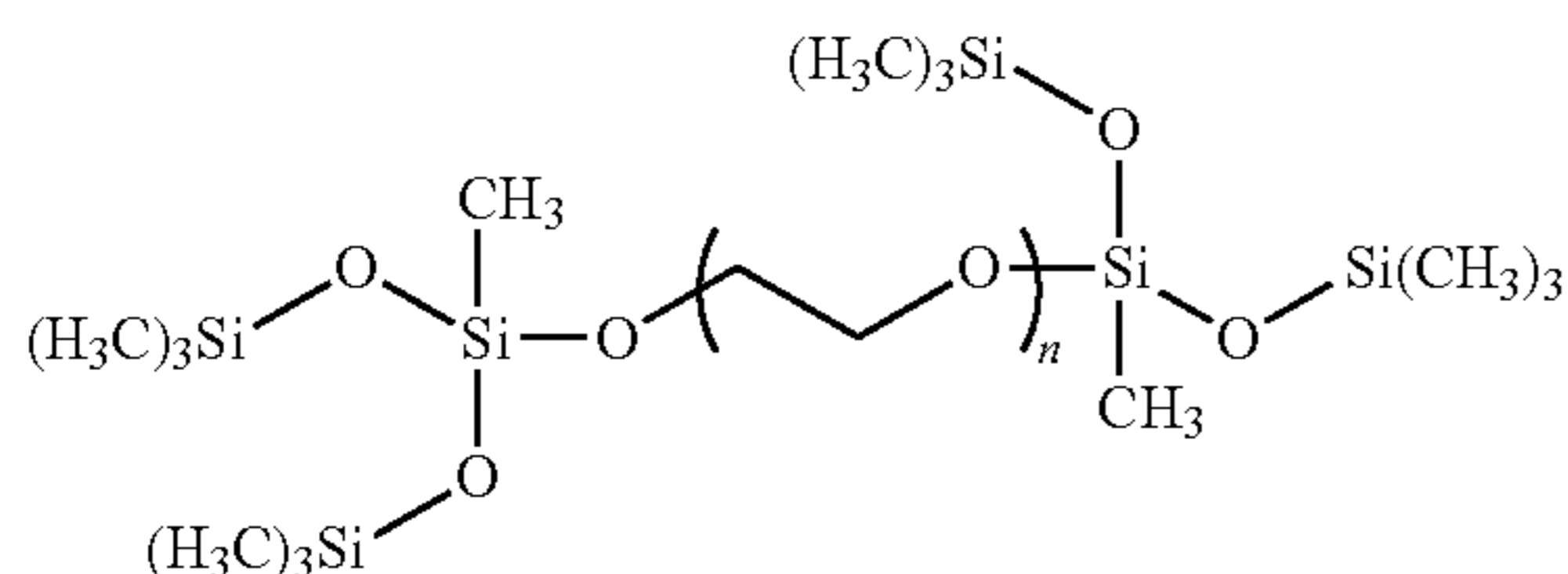
Formula VII-A



Formula VII-B



Formula VII-C



Formula VII-D

In each of the formulas, each n is independently an integer from 1 to 12.

Formula VII-A illustrates a trisiloxane where the central silicon atom is directly linked to a side chain that includes a poly(ethylene oxide). Formulas VII-C and VII-D illustrate trisiloxanes having a central silicon atom linked through a cross-link (e.g. the poly(alkylene oxide) moiety) joining the trisiloxane to a second trisiloxane. Formula VII-C illustrates the cross-link including a spacer positioned between the poly(alkylene oxide) moiety and each of the trisiloxanes. Formula VII-D illustrates a silicon atom in the backbone of each trisiloxane linked directly to a poly(alkylene oxide) moiety. In some embodiments, the trisiloxane is $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$,

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$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_3)_2\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$; $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$; $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_3$, $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_4$, $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_5$, $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_6$, $(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_7$; $(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2)_n\text{CH}_3$, or a mixture of any two or more such compounds, where n is 2, 3, 4, 5, 6, or 7, and R is a carbonate group.

To the extent they are not specifically described above, illustrative monosiloxanes include, but are not limited to, $\text{Si}(\text{CH}_3)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $\text{Si}(\text{CH}_3)_3\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $\text{Si}(\text{CH}_3)_3(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, $\text{Si}(\text{CH}_3)_2[\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3]_2$, $\text{SiCH}_3[\text{O}(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_3]_3$, $\text{Si}[\text{O}(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_3]_4$, $\text{Si}(\text{CH}_3)_2[\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3]$, $(\text{CH}_2)_3\text{OR}$, or $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{OR}$, R is a carbonate group, n is 2, 3, 4, 5, 6, or 7, n' is 2, 3, 4, or 5, p is 2, 3, or 4; and p' is 2 or 3. To the extent they are not specifically described above, illustrative disiloxanes include, but are not limited to, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{OR}$; $\text{ROSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OR}$; $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{OR}$; or $\text{RO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{OR}$, where n is 2, 3, 4, 5, 6, or 7; and R is a carbonate group. To the extent they are not specifically described above, illustrative trisiloxanes include, but are not limited to, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{O}(\text{CH}_3)_2\text{Si}-(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)[\text{OSi}(\text{CH}_3)_3]_2$, $\text{ROSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OR}$, $\text{ROSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$; $\text{RO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{OR}$, $\text{RO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$; $\text{RO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2)_n\text{CH}_3$ or $\text{RO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2)_n\text{CH}_3$, where n is 2, 3, 4, 5, 6, or 7; and R is a carbonate group.

tionalized ammoniums, protonated ammoniums, and cholines. Suitable phosphoniums include symmetrical phosphoniums and unsymmetrical phosphoniums. The anion of the RTILs may include, but are not limited to, $[\text{CF}_3\text{CO}_2]^-$; $[\text{C}_2\text{F}_5\text{CO}_2]^-$; $[\text{ClO}_4]^-$; $[\text{BF}_4]^-$; $[\text{AsF}_6]^-$; $[\text{PF}_6]^-$; $[\text{PF}_2(\text{C}_2\text{O}_4)_2]^-$; $[\text{PF}_4\text{C}_2\text{O}_4]^-$; $[\text{CF}_3\text{SO}_3]^-$; $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$; $[\text{C}(\text{CF}_3\text{SO}_2)_3]^-$; $[\text{N}(\text{SO}_2\text{C}_2\text{F}_5)_2]^-$; alkyl fluorophosphates; $[\text{B}(\text{C}_2\text{O}_4)_2]^-$; $[\text{BF}_2\text{C}_2\text{O}_4]^-$; $[\text{B}_{12}\text{X}_{12-k}\text{H}_k]^{2-}$; $[\text{B}_{10}\text{X}_{10-k}\text{H}_k]^{2-}$; or a combination of any two or more thereof.

The electrolyte may be a liquid, a gel, or a solid. For instance, the electrolyte can include a porous phase that absorbs a liquid electrolyte. The porous phase can provide the structure needed for the electrolyte to be a gel or solid. The porous phase can include or consist of a copolymer and one or more silicon compounds that are each selected from a group consisting of silanes and siloxanes. Suitable siloxanes include, but are not limited to, the polysiloxanes, tetrasiloxanes, trisiloxanes, and disiloxanes disclosed above. The copolymer and the one or more silicon compounds can be microphase separated in the porous phase. The liquid electrolyte can include one or more of the above salts dissolved in a liquid solvent. The liquid solvent can include one or more of the above organic solvents and/or one or more of the above siloxanes and/or one or more of the above silanes.

In some other embodiments, the electrolyte includes an aprotic gel polymer carrier/solvent. Suitable gel polymer carrier/solvents include polyethers, polyethylene oxides, polyimides, polyphosphazines, polyacrylonitriles, polysiloxanes, polyether grafted polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, cross-linked and network structures of the foregoing, blends of the foregoing, and the like, to which is added an appropriate ionic electrolyte salt. Other gel-polymer carrier/solvents include those prepared from polymer matrices derived from polypropylene oxides, polysiloxanes, sulfonated polyimides, perfluorinated membranes (Nafion resins), divinyl polyethylene glycols, polyethylene glycol-bis-(methyl acrylates), polyethylene glycol-bis(methyl methacrylates), derivatives of the foregoing, copolymers of the foregoing, cross-linked and network structures of the foregoing.

In another aspect, an electrochemical device is provided that includes a cathode; an anode; and any of the above electrolytes. The hybrid additive forms a passivation layer on at least one anode and/or one at least one cathode. The hybrid additives of the first and second compounds described above have been found to stabilize the surface of carbonaceous anode and increase the capacity and/or the cycling capabilities of the disclosed batteries. The combination of first and second compound provides for a synergistic effect over the effects of the additives when used singly. Such a hybrid additive forms an SEI with low impedance and offer high rate capability. The electrochemical device may be a lithium secondary battery such as a lithium battery, a lithium-ion battery, a lithium-sulfur battery, a lithium-air battery, a sodium ion battery, or a magnesium battery. The electrochemical device may be a capacitor. For example, the capacitor may be an asymmetric capacitor or supercapacitor. In some embodiments, the electrochemical cell is a primary cell. In some embodiments, the primary cell that is a lithium/MnO₂ battery or Li/poly(carbon monofluoride) battery. In some embodiments, the electrochemical cell is a solar cell.

Suitable cathodes include those such as, but not limited to, a lithium metal oxide, spinel, olivine, carbon-coated olivine, LiFePO₄, LiCoO₂, LiNiO₂, LiNi_{1-x}Co_yMet_zO₂, LiMn_{0.5}Ni_{0.5}O₂, LiMn_{0.3}CO_{0.3}Ni_{0.3}O₂, LiMn₂O₄, LiFeO₂, Li_{1+x}Ni_αMn_βCo_γMet'_δO_{2-z}F_z, A_nB₂(XO₄)₃ (NASICON), vanadium oxide, lithium peroxide, sulfur, polysulfide, a

lithium carbon monofluoride (also known as LiCFx), or mixtures of any two or more thereof, where Met is Al, Mg, Ti, B, Ga, Si, Mn, or Co; Met' is Mg, Zn, Al, Ga, B, Zr, or Ti; A is Li, Ag, Cu, Na, Mn, Fe, Co, Ni, Cu, or Zn; B is Ti, V, Cr, Fe, or Zr; X is P, S, Si, W, or Mo; $0 \leq x \leq 0.3$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$; $0 \leq x' \leq 0.4$, $0 \leq \alpha \leq 1$, $0 \leq \beta \leq 1$, $0 \leq \gamma \leq 1$, $0 \leq \delta \leq 0.4$, and $0 \leq z' \leq 0.4$; and $0 \leq n \leq 3$. According to some embodiments, the spinel is a spinel manganese oxide with the formula of Li_{1+x}Mn_{2-z}Met'''_yO_{4-m}X'_n, wherein Met''' is Al, Mg, Ti, B, Ga, Si, Ni, or Co; X' is S or F; and wherein $0 \leq x \leq 0.3$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, $0 \leq m \leq 0.5$ and $0 \leq n \leq 0.5$. In other embodiments, the olivine has a formula of Li_{1+x}Fe_{1-z}Met''_yPO_{4-m}X'_n, wherein Met'' is Al, Mg, Ti, B, Ga, Si, Ni, Mn or Co; X' is S or F; and wherein $0 \leq x \leq 0.3$, $0 \leq y \leq 0.5$, $0 \leq z \leq 0.5$, $0 \leq m \leq 0.5$ and $0 \leq n \leq 0.5$.

Suitable anodes include those such as lithium metal; graphitic materials, amorphous carbon, Li₄Ti₅O₁₂, tin alloys, silicon alloys, intermetallic compounds, or mixtures of any two or more such materials. Suitable graphitic materials including natural graphite, artificial graphite, graphitized meso-carbon microbeads (MCMB), and graphite fibers, as well as any amorphous carbon materials.

The anode and cathode may be separated from each other by a porous separator. The separator for the lithium battery may be a microporous polymer film. Examples of polymers for forming films include: nylon, cellulose, nitrocellulose, polysulfone, polyacrylonitrile, polyvinylidene fluoride, polypropylene, polyethylene, polybutene, or co-polymers or blends of any two or more such polymers. In some instances, the separator is an electron beam treated micro-porous polyolefin separator. The electron treatment can improve the deformation temperature of the separator and can accordingly enhance the high temperature performance of the separator. Additionally, or alternatively, the separator can be a shut-down separator. The shut-down separator can have a trigger temperature above 130° C. to permit the electrochemical cells to operate at temperatures up to 130° C.

Such electrochemical devices and batteries are not limited to particular shapes, and can take any appropriate shape such as cylindrical shape, a coin shape, and a square shape. The batteries also are not limited to particular capacities, and can have any appropriate capacity for both small appliances and power storage or electric cars.

As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a

shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

As used herein, “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, “about” will mean up to plus or minus 10% of the particular term.

All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising,” “including,” “containing,” etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Additionally the phrase “consisting essentially of” will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed invention. The phrase “consisting of” excludes any element not specifically specified. In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

One skilled in the art will readily realize that all ranges discussed can and do necessarily also describe all subranges therein for all purposes and that all such subranges also form part and parcel of this invention. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc.

All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

The present invention, thus generally described, will be understood more readily by reference to the following

examples, which are provided by way of illustration and are not intended to be limiting of the present invention.

EXAMPLES

Example 1

A 2032 coin cell was assembled with a cathode of LiMn_2O_4 , an anode of massive artificial graphite (MAG), and an electrolyte including 1.0 M LiPF_6 in 2-[2-[2-[2-methoxy]ethoxy]ethoxy]ethoxy trimethyl silane (1NM3). The coin cell was cycled at a charging rate of C/10 (0.2 mA), and C/10 for discharge. FIG. 1 is a graph illustrating that the electrolyte is unstable in the cell due to the lack of stable SEI formation.

Example 2

A 2032 coin cell was assembled with LiMn_2O_4 as cathode, MAG as anode, and an electrolyte including a solvent of 1NM3 with 1.0M LiPF_6 , and 2 wt % VC, LiBOB, or LiDfOB. The coin cell was cycled at a charging rate of C/10 (0.2 mA), and C/10 for discharge. FIG. 2 illustrates that with a single additive, the silane based electrolyte was unstable in the cell due to the lack of stable SEI formation.

Example 3

A 2032 coin cell was assembled with LiMn_2O_4 as cathode, MAG as anode, and an electrolyte including a solvent of 1NM3 with 1.0M LiPF_6 , and 2 wt % VC and 2 wt % LiBOB. The coin cell was cycled at a charging rate of C/10 (0.2 mA), and C/10 for discharge. FIG. 3 illustrates that with the hybrid (dual) additive, the silane-based electrolyte forms a very stable SEI on the surface of graphite anode, thereby preventing the reductive decomposition of the silane solvent. Excellent cycling performance was achieved for silane electrolyte with the hybrid additive.

Example 4

A 2032 coin cell was assembled with LiMn_2O_4 as cathode, MAG as anode, and an electrolyte including a solvent of 1NM3 with 1.0M LiPF_6 , and 2 wt % VC and 2 wt % PC. The coin cell was cycled at a charging rate of C/10 (0.2 mA), and C/10 for discharge. FIG. 4 illustrates that with the hybrid (dual) additive, the silane-based electrolyte forms a very stable SEI on the surface of graphite anode, thereby preventing the reductive decomposition of the silane solvent. Excellent cycling performance was achieved for silane electrolyte with the hybrid additive.

Example 5

A 2032 coin cell was assembled with LiMn_2O_4 as cathode, MAG as anode, and an electrolyte including a solvent of 1NM3 with 1.0M LiPF_6 , and 2 wt % VC and 2 wt % LiBOB. The coin cell was cycled at a charging rate of C/10 (0.2 mA), and C/10 for discharge. FIG. 5 illustrates that a very high Columbic efficiency may be achieved with the hybrid additive. The hybrid (dual) additive, the silane-based electrolyte forms a very stable SEI on the surface of graphite anode, thereby preventing the reductive decomposition of the silane solvent. Excellent cycling performance was achieved for silane electrolyte with the hybrid additive. FIG. 5 also illustrates the difference between single additive electrolytes and the hybrid additive electrolyte. For example, with either 2 wt % VC or 2 wt % LiBOB, alone, the efficiency is low, however

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when both 2 wt % VC and 2 wt % LiBOB are used, the efficiency is very high (>99%). This is a surprising finding.

While various aspects and embodiments have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

What is claimed is:

1. An electrochemical device comprising:

an anodic material; and

an electrolyte, the electrolyte comprising:

a hybrid additive comprising a first compound and propylene carbonate, the hybrid additive configured to form a solid electrolyte interphase film on the anodic material upon application of a potential to the electrochemical device;

a salt comprising LiBr, LiI, LiSCN, LiBF₄, LiAlF₄, LiPF₆, LiAsF₆, LiClO₄, Li₂SO₄, LiB(Ph)₄, LiAlO₂, Li[N(FSO₂)₂], Li[SO₃CH₃], Li[BF₃(C₂F₅)], Li[PF₃(CF₂CF₃)₃], Li[B(C₂O₄)₂], Li[B(C₂O₄)F₂], Li[PF₄(C₂O₄)], Li[PF₂(C₂O₄)₂], Li[CF₃CO₂], Li[C₂F₅CO₂], Li[N(CF₃SO₂)₂], Li[C(SO₂CF₃)₃], Li[N(C₂F₅SO₂)₂], Li[CF₃SO₃], Li₂B₁₂X_{12-n}H_n, Li₂B₁₀X_{10-n}H_n, Li₂S_xⁿ, (LiS_xⁿR¹)_y, or lithium alkyl fluorophosphates; where X is a halogen, n is an integer from 0 to 12, n' is an integer from 0 to 10, x" is an integer from 1 to 20, y is an integer from 1 to 3, and R¹ is H, alkyl, alkenyl, aryl, ether, F, CF₃, COCF₃, SO₂CF₃, or SO₂F; and

a non-aqueous solvent comprising Si(CH₃)₃O(CH₂CH₂O)_nCH₃, Si(CH₃)₃CH₂O(CH₂CH₂O)_nCH₃, Si(CH₃)₃(CH₂)₃O(CH₂CH₂O)_nCH₃, Si(CH₃)₂[O(CH₂CH₂O)_nCH₃]₂, CH₃Si[O(CH₂CH₂O)_pCH₃]₃, Si[O(CH₂CH₂O)_pCH₃]₄, Si(CH₃)₂[O(CH₂CH₂O)_nCH₃][(CH₂)₃O(CH₂CH₂O)_nCH₃], (CH₃)₃SiOR, or (CH₃)₃Si(CH₂)₃OR;

wherein:

R is a carbonate group;

n is 2, 3, 4, 5, 6, or 7;

n' is 2, 3, 4, or 5;

p is 2, 3, or 4; and

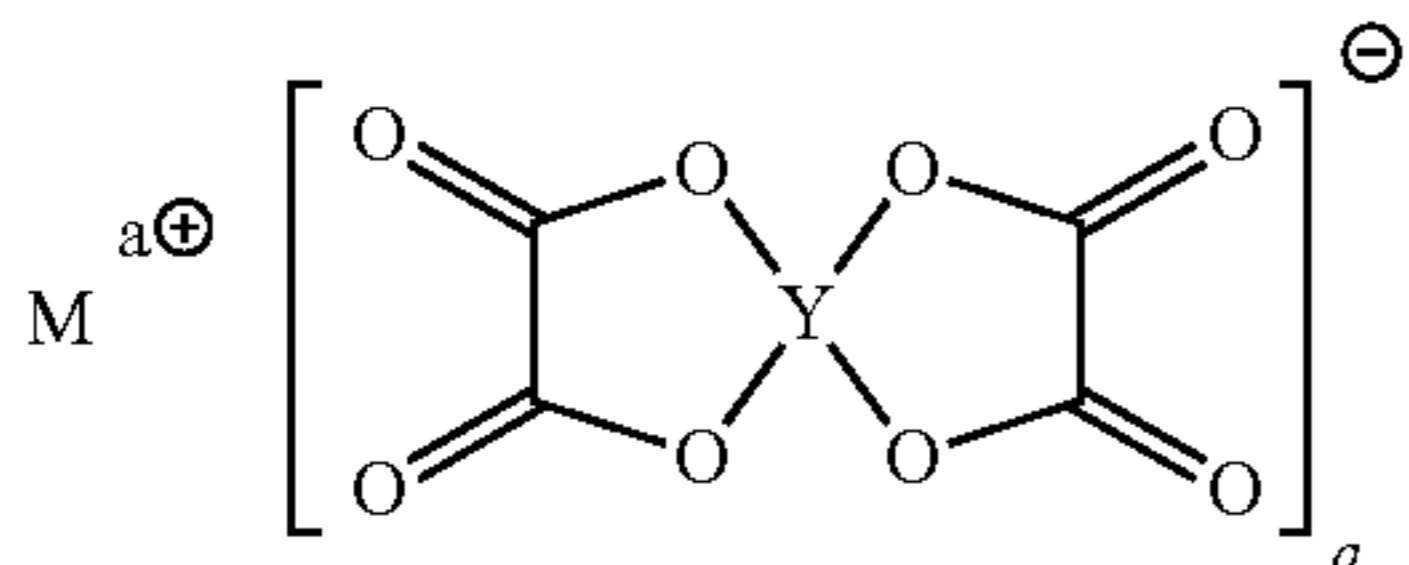
p' is 2 or 3;

wherein:

the electrolyte comprises about 1 wt % to about 3 wt % of the first compound;

the electrolyte comprises about 1 wt % to about 3 wt % of the propylene carbonate;

the first compound is represented by Formula I-B:



M is a metal ion, an ammonium, a phosphonium, a sulfonium, an imidazolium, a pyridinium, or trityl;

a is 1, 2, 3, or 4; and

Y is B.

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2. The electrochemical device of claim 1, wherein the electrolyte comprises about 2 wt % of the first compound, and about 2 wt % of the second compound.

3. The electrochemical device of claim 1, wherein M is Li⁺, Na⁺, or K⁺.

4. The electrochemical device of claim 1, wherein the anode comprises graphite, amorphous carbon, Li₄Ti₅O₁₂, a tin alloy, a silicon alloy, an intermetallic compound, or lithium metal.

5. The electrochemical device of claim 1 further comprising a separator.

6. A non-aqueous electrolyte comprising:

a first compound; a second compound;

a salt comprising LiBr, LiI, LiSCN, LiBF₄, LiAlF₄, LiPF₆, LiAsF₆, LiClO₄, Li₂SO₄, LiB(Ph)₄, LiAlO₂, Li[N(FSO₂)₂], Li[SO₃CH₃], Li[BF₃(C₂F₅)], Li[PF₃(CF₂CF₃)₃], Li[B(C₂O₄)F₂], Li[PF₄(C₂O₄)], Li[PF₂(C₂O₄)₂], Li[CF₃CO₂], Li[C₂F₅CO₂], Li[N(CF₃SO₂)₂], Li[C(SO₂CF₃)₃], Li[N(C₂F₅SO₂)₂], Li[CF₃SO₃], Li₂B₁₂X_{12-n}H_n, Li₂B₁₀X_{10-n}H_n, Li₂S_xⁿ, (LiS_xⁿR¹)_y, or lithium alkyl fluorophosphates; where X is a halogen, n is an integer from 0 to 12, n' is an integer from 0 to 10, x" is an integer from 1 to 20, y is an integer from 1 to 3, and R¹ is H, alkyl, alkenyl, aryl, ether, F, CF₃, COCF₃, SO₂CF₃, or SO₂F; and

a non-aqueous solvent comprising Si(CH₃)₃O(CH₂CH₂O)_nCH₃, Si(CH₃)₃CH₂O(CH₂CH₂O)_nCH₃, Si(CH₃)₃(CH₂)₃O(CH₂CH₂O)_nCH₃, Si(CH₃)₂[O(CH₂CH₂O)_nCH₃]₂, Si(CH₃)₃[O(CH₂CH₂O)_pCH₃]₃, Si[O(CH₂CH₂O)_pCH₃]₄, Si(CH₃)₂[O(CH₂CH₂O)_nCH₃][(CH₂)₃O(CH₂CH₂O)_nCH₃], (CH₃)₃SiOR, or (CH₃)₃Si(CH₂)₃OR;

wherein:

R is a carbonate group;

n is 2, 3, 4, 5, 6, or 7;

n' is 2, 3, 4, or 5;

p is 2, 3, or 4; and

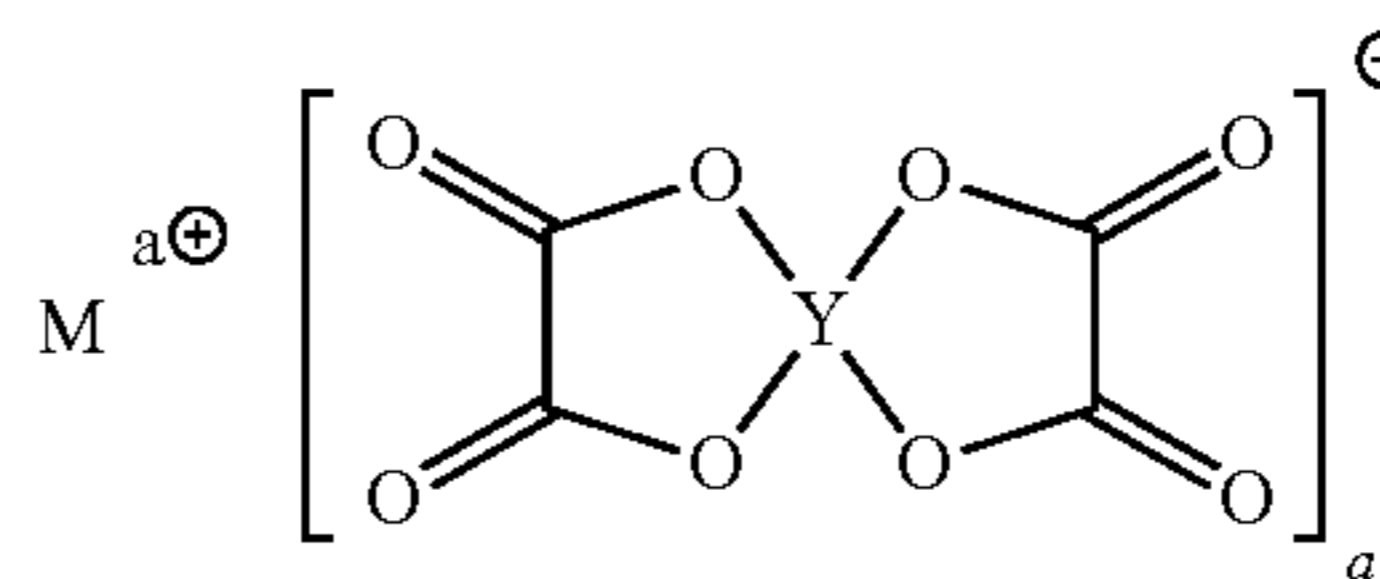
p' is 2 or 3;

wherein:

the electrolyte comprises about 1 wt % to about 3 wt % of the first compound;

the electrolyte comprises about 1 wt % to about 3 wt % of the second compound;

the first compound is represented by Formula I-B:



the second compound is propylene carbonate;

M is a metal ion, an ammonium, a phosphonium, a sulfonium, an imidazolium, a pyridinium, or trityl;

a is 1, 2, 3, or 4; and

Y is B.

7. The non-aqueous electrolyte of claim 6, wherein the electrolyte comprises about 2 wt % of the first compound, and about 2 wt % of the second compound.

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